



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/00540 <b>(22) International Filing Date:</b> 8 January 1999 (08.01.99) <b>(30) Priority Data:</b> 60/071,050 9 January 1998 (09.01.98) US <b>(71) Applicant (for all designated States except US):</b> THE BOARD OF TRUSTEES OF THE LELAND STANFORD JR. UNIVERSITY [US/US]; Suite 350, 900 Welch Road, Palo Alto, CA 94304-1850 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> WAYMOUTH, Robert, M. [US/US]; 420 Alger Drive, Palo Alto, CA 94306 (US). KRAVCHENKO, Raisa, L. [RU/US]; 5525 Limeric Circle #44, Wilmington, DE 19808 (US). MACIEJEWSKI PETOFF, Jennifer [US/US]; 390 Ano Nuevo Avenue #710, Sunnyvale, CA 94086 (US). <b>(74) Agent:</b> DULIN, Jacques, M.; Heller Ehrman White & McAuliffe, 525 University Avenue, Palo Alto, CA 94301-1900 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HIGH-MELTING POLYOLEFIN COPOLYMER ELASTOMERS, CATALYSTS AND METHODS OF SYNTHESIS		
<b>(57) Abstract</b>		
<p>This invention relates to high melting polyolefin copolymers suitable as thermoplastic elastomers and catalysts and methods for their synthesis. These elastomeric olefin copolymers are characterized by a mole fraction of crystallizable component X<sub>C</sub> from about 30 to about 99 %; low glass transition temperatures, below -20 °C, and typically below -50 °C; melting points above about 90 °C; high molecular weights; a molecular weight distribution M<sub>w</sub>/M<sub>n</sub> ≤ 10; and a narrow composition distribution between chains of ≤ 15 %. The novel copolymers of the invention range from reactor blends to multiblock copolymers that can be sequentially fractionated into fractions of differing crystallinities, which fractions nevertheless show compositions of comonomers which differ by less than 15 % from the parent polymer (reactor product). The invention also relates to a process for producing such copolymers by utilizing an unbridged, substituted or unsubstituted cyclopentadienyl metallocene catalyst that is capable of interconverting between states with different copolymerization characteristics, which interconversion is controlled by selecting the substituents of the cyclopentadienyl ligands so that the rate of interconversion of the two states is within several orders of magnitude of the rate of formation of a single polymer chain. Where r<sub>i</sub> &gt; r<sub>f</sub> the polymer can be characterized as multiblock; where r<sub>i</sub> &lt; r<sub>f</sub>, the result is a polymer blend and where r<sub>i</sub>/r<sub>f</sub> is close to 1, the resulting polymer is a mixture of blend and multiblock. The metallocene catalysts of the invention are able to interconvert between more than two states, with embodiments of four states being shown in Figure 2.</p>		

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**TITLE: HIGH-MELTING POLYOLEFIN COPOLYMER ELASTOMERS,  
CATALYSTS AND METHODS OF SYNTHESIS**

**DESCRIPTION**

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**CROSS REFERENCE TO RELATED APPLICATIONS:**

This application is the regular application of an earlier filed Provisional application Serial Number 60/071,050, entitled Catalyst and Process for Synthesis of Olefin Block Copolymers, filed January 9, 1998 by Waymouth and Kravchenko, the benefit of the filing date of which is hereby claimed under 35 U.S. Code §§ 112, 119(e) and 120, and under appropriate provisions of the PCT rules.

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**TECHNICAL FIELD:**

This invention relates to high melting polyolefin copolymers suitable as thermoplastic elastomers and catalysts and methods for their synthesis. These olefin copolymers are characterized by low glass transition temperatures, melting points above about 90°C, high molecular weights, and a narrow composition distribution between chains. The copolymers of the invention are novel reactor blends that can be sequentially fractionated into fractions of differing crystallinities, said fractions nevertheless show compositions of comonomers which differ by less than 15% from the parent reactor blend. The invention also relates to a process for producing such copolymers by utilizing an unbridged metallocene catalyst that is capable of interconverting between states with different copolymerization characteristics.

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**BACKGROUND:**

Ethylene alpha-olefin copolymers are important commercial products. These copolymers find a particularly broad range of application as elastomers. There are generally three family of elastomers made from such copolymers. One class is typified by ethylene-propylene copolymers (EPR) which are saturated compounds, optimally of low crystallinity, requiring vulcanization with free-radical generators to achieve excellent elastic properties. Another type of elastomer is typified by ethylene-propylene terpolymers (EPDM), again optimally of low crystallinity, which contain a small amount of a non-conjugated diene such as ethylidene norbornene. The residual unsaturation provided by the

35

diene termonomomer allows for vulcanization with sulfur, which then yields excellent elastomeric properties. Yet another class is typified by ethylene-alpha olefin copolymers of narrow composition distribution which possess excellent elastomeric properties even in the absence of vulcanization. For example US Patent 5,278,272, to Dow describes a class of substantially linear polyolefin copolymer elastomers with narrow composition distribution and excellent processing characteristics. (These latter class of elastomers are typified for example by the EXACT<sub>™</sub> and ENGAGE<sub>™</sub> brand products sold commercially by Exxon and Dow, respectively.) One of the limitations of the latter class of elastomers is the low melting temperature of these materials which limits their high temperature performance.

Hence it would be extremely advantageous to industry to produce copolymers of ethylene and alpha olefins which would show both elastomeric properties in the unvulcanized state and high melting points.

## THE INVENTION

### SUMMARY, OBJECTS AND ADVANTAGES:

It is among the objects of this invention to provide methods of production of a class of novel polyolefin copolymers with a combination of interesting and useful physical characteristics, including a molecular weight distribution,  $M_w/M_n \leq 10$ , a narrow composition distribution,  $\leq 15\%$ , high melting point index, melting points greater than about 90°C and elastomeric properties. It is a further object of this invention to produce a novel family of crystallizable, high-melting polyolefin copolymers having a narrow composition distribution where the melting point of the polymer is greater than about 90°C. It is a further object of this invention to produce a class of high-melting, multiblock, blend, and multiblock/blend polyolefin copolymer elastomers. These novel polymers are useful as elastomeric and/or thermoplastic materials as well as compatibilizers for other polyolefin blends.

We have unexpectedly found that it is possible to prepare high melting polyolefin elastomers of narrow composition distribution using novel unbridged metallocenes as olefin polymerization catalysts. For convenience, certain terms used throughout the specification are defined below (with " $\leq$ " or " $\geq$ " meaning less than or equal to, or greater than or equal to):

a. "Multiblock" polymer or copolymer means a polymer comprised of multiple block sequences of monomer units where the structure or composition of a given sequence differs from that of its neighbor. Furthermore a multiblock copolymer as defined herein will contain a given sequence at least twice in every polymer chain.

b. The term "composition distribution" refers to the variation in comonomer composition between different polymer chains and can be described as a difference, in mole percent, of a given weight percent of a sample from the mean mole percent composition.

The distribution need not be symmetrical around the mean; when expressed as a number, for example 15%, this shall mean the larger of the distributions from the mean.

c. As used herein, the term "elastomeric" refers to a material which tends to regain its shape upon extension, such as one which exhibits a positive power of recovery at 100,  
5 200 and 300% elongation.

d. The term "melting point index", also referred-to as  $MPI = T_m / X_c$ , means the ratio of the melting point of the copolymer,  $T_m$ , to the mole fraction of the crystallizable component,  $X_c$ . By crystallizable component, we mean a monomer component whose homopolymer is a crystalline polymer. The melting point is taken as a maximum in a  
10 melting endotherm, as determined by differential scanning calorimetry.

The copolymers of the present invention have the following characteristics:

- (a) a mole fraction of crystallizable component  $X_c$  from 30 - 99%;
- (b) a molecular weight distribution  $M_w / M_n \leq 10$ ; and
- (c) melting points above about 90°C;

15 which copolymers comprise from 0-70% by weight of an ether soluble fraction, and from 0-95% of a hexanes soluble fraction which can exhibit a melting range up to about 125°C, and from 0-95% of a hexanes insoluble fraction which can exhibit a melting range up to about 142°C.

The copolymers of the present invention in one embodiment can be characterized as  
20 reactor blends in that they can be fractionated into fractions of differing degrees of crystallinity and differing melting points. Nevertheless, the comonomer composition of the various fractions of the copolymers are within 15% of the composition of the resultant polymer product produced in the reactor.

The melting points of the copolymers of the present invention are high, typically  
25 above 90 °C and the melting point indices,  $T_m / X_c$  are also high, typically above 80 °C and preferably above 115°C. The fractions can also exhibit high melting point indices. For example, it is possible to isolate a hexanes soluble fraction from the copolymers of the present invention that exhibits a melting point as high as 115 °C and a melting point index as high as 160 °C. The glass transition temperatures of the copolymers are low, typically  
30 less than -20 °C and preferably below -50 °C.

The molecular weights of the polymers of the present invention can be quite high, with weight average molecular weights in excess of  $M_w = 1,000,000$  readily obtained and molecular weights as high as 2,000,000 observed. The molecular weight distributions of the copolymers are typically  $M_w / M_n \leq 10$ , preferably  $M_w / M_n \leq 8$  and most  
35 preferably  $\leq 6$ .



In one embodiment, the copolymers of the present invention exhibit useful elastomeric properties. They can be used in a variety of applications typical of amorphous or partially crystalline elastomers and as compatibilizers for copolymer blends.

While not wishing to be bound by theory, it is believed that in the process of the invention, different active species of the catalyst are in equilibrium during the construction of the copolymer chains. This is provided for in the present invention by a class of unbridged metallocenes that are capable of isomerizing between states that have different copolymerization characteristics during the polymerization process. This process can thus lead to multiblock copolymers or copolymer blends where the blocks or components of the blends have different compositions of comonomers.

One embodiment of the invention includes metallocene catalysts which are able to interconvert between states whose coordination geometries are different. Thus, the invention includes selecting the substituents of the metallocene cyclopentadienyl ligands so that the rate of interconversion of the two states is within several orders of magnitude of the rate of formation of a single polymer chain. That is, if the rate of interconversion between states of the catalyst,  $r_i$ , is greater than the rate of formation of an individual polymer chain,  $r_f$ , on average, the polymer resulting from use of the inventive process and catalysts can be characterized as multiblock (as defined above). If the rate of interconversion is less than the rate of formation, the result is a polymer blend. Where the rates are substantially balanced, the polymer can be characterized as a mixture of blend and multiblock. There may be a wide range of variations and intermediate cases amongst these three exemplars.

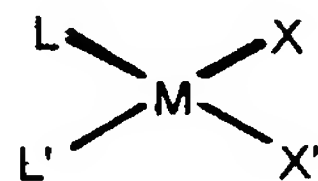
The nature of the substituents on the cyclopentadienyl ligands is critical; the substitution pattern of the cyclopentadienyl ligands should be such that the coordination geometries are different in order to provide for different reactivities toward ethylene and other alpha olefins while in the two states (see Figure 1) and that the rate of interconversion of the states of the catalyst are within several orders of magnitude of the rate of formation of a single chain.

A further embodiment includes metallocene catalysts which are able to interconvert between more than two states whose coordination geometries are different. This is provided for by metallocenes with cyclopentadienyl-type ligands substituted in such a way that more than two stable states of the catalyst have coordination geometries that are different, for example, a catalyst with four geometries is illustrated in one embodiment in Figure 2.

According to the process of this invention, the properties of the copolymers can be controlled by changing the nature of the cyclopentadienyl units on the catalysts, by changing the nature of the metal atom in the catalyst, by changing the nature of the comonomers and the comonomer feed ratio, and by changing the temperature.

The molecular weights of the polymers produced with the catalysts of the invention are very high. The molecular weight of the polymer product can be controlled, optionally, by controlling the temperature or by adding any number of chain transfer agents such as hydrogen or metal alkyls, as is well known in the art.

5 The catalyst system of the present invention consists of the transition metal component metallocene in the presence of an appropriate cocatalyst. In broad aspect, the transition metal compounds have the formula:

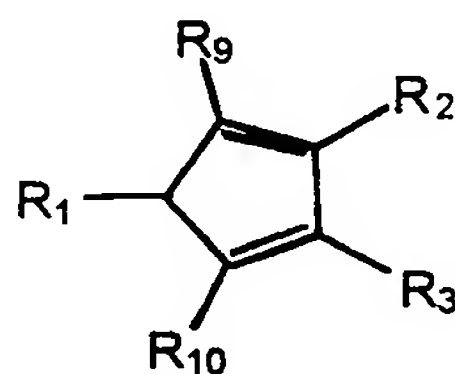


Formula 1

10

in which M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide, X and X' are the same or different uninegative ligands, such as but not limited to hydride, halogen, hydrocarbyl, halohydrocarbyl, amine, amide, or borohydride substituents (preferably halogen, alkoxide, or C<sub>1</sub> to C<sub>7</sub> hydrocarbyl), and L and L' are the same or different  
15 polynuclear hydrocarbyl, silahydrocarbyl, phosphahydrocarbyl, azahydrocarbyl, arseni-hydrocarbyl or borahydrocarbyl rings, typically a substituted cyclo-pentadienyl ring or heterocyclopentadienyl ring, in combination with an appropriate cocatalyst. Exemplary preferred Transition Metals include Titanium, Hafnium, Vanadium, and, most preferably, Zirconium. An exemplary Group 3 metal is Yttrium, a Lanthanide is Samarium, and an  
20 Actinide is Thorium.

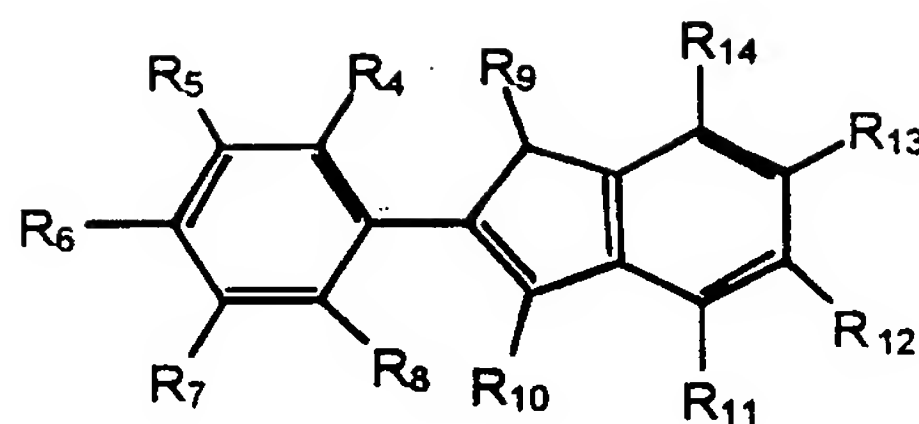
Preferably L and L' have the formula:



Formula 2

25 where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>9</sub>, and R<sub>10</sub> may be the same or different hydrogen, alkyl, alkylsilyl, aryl, alkoxyalkyl, alkoxyaryl, alkoxyalkyl, aminoalkyl, aminoaryl or substituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms.

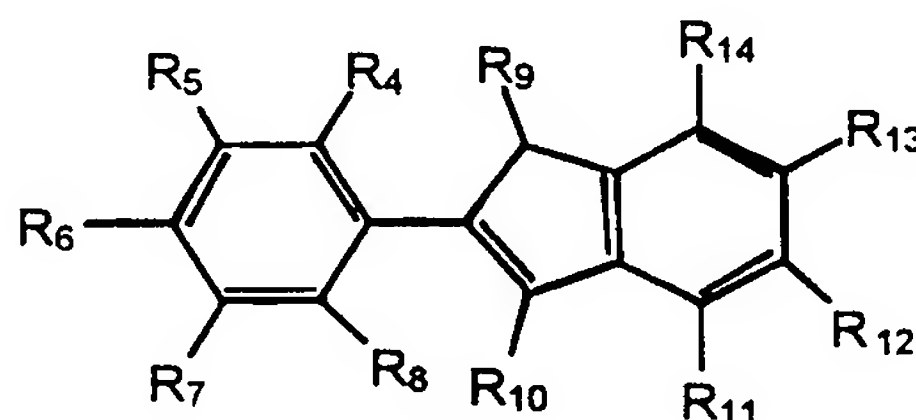
Ligands of this general structure include substituted cyclopentadienes. Other ligands L and L' of Formula 2 for the production of propylene-ethylene copolymers include  
30 substituted cyclopentadienes of the general formula:



Formula 3

where R<sub>2</sub>-R<sub>10</sub> have the same definition as R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>9</sub>, and R<sub>10</sub> above. Preferred  
 5 cyclopentadienes of Formula 3 include 3,4-dimethyl-1-phenyl-1,3-cyclopentadiene  
 (R<sub>2</sub>=R<sub>3</sub>=CH<sub>3</sub>, R<sub>6</sub>=H); 3,4-dimethyl-1-p-tolyl-1,3-cyclopentadiene (R<sub>2</sub>=R<sub>3</sub>=CH<sub>3</sub>,  
 R<sub>6</sub>=CH<sub>3</sub>); 3,4-dimethyl-1-(3,5-bis(trifluoromethyl)phenyl)-1,3-cyclopentadiene (R<sub>2</sub>=R<sub>3</sub>  
 =CH<sub>3</sub>, R<sub>6</sub>=CF<sub>3</sub>); and 3,4-dimethyl-1-(4-*tert*-butylphenyl)-1,3-cyclopentadiene (R<sub>2</sub>=R<sub>3</sub>  
 =CH<sub>3</sub>, R<sub>6</sub>=tBu).

10 Alternately preferred L and L' of Formula 1 include ligands of Formula 2 wherein  
 R<sub>1</sub> is an aryl group, such as a substituted phenyl, biphenyl, or naphthyl group, and R<sub>2</sub> and  
 R<sub>3</sub> are connected as part of a ring of three or more carbon atoms. Especially preferred for  
 L or L' of Formulas 1- 3 for producing the copolymers of this invention are substituted  
 indenyl ligands, more particularly 2-arylidene of formula:



Formula 4

where R<sub>4</sub> - R<sub>14</sub> may be the same or different hydrogen, halogen, aryl, hydrocarbyl,  
 silahydrocarbyl, or halohydrocarbyl substituents. That is, R<sub>1</sub> of Formula 2 is R<sub>4</sub>-R<sub>8</sub>-  
 20 substituted benzene, and R<sub>2</sub>, R<sub>3</sub> are cyclized in a 6-carbon ring to form the indene moiety.

Particularly preferred 2-aryl indenenes include at present as preferred best mode  
 compounds: 2-phenylindene; 1-methyl-2-phenyl indene; 2-(3,5-dimethylphenyl) indene; 2-  
 (3,5-bis-trifluoromethylphenyl) indene; 1-methyl-2-(3,5-bis-trifluoromethylphenyl) indene;  
 2-(3,5-bis-*tert*butylphenyl) indene; 1-methyl-2-(3,5-bis-*tert*butylphenyl) indene; 2-(3,5-bis-  
 25 trimethyl- silylphenyl)indene; 1-methyl-2-(3,5-bis-trimethylsilylphenyl)indene; 2-(4-  
 fluorophenyl) indene; 2-(2, 3, 4, 5-tetrafluorophenyl) indene; 2-(2, 3, 4, 5, 6-  
 pentafluorophenyl) indene; 2-(1-naphthyl) indene; 2-(2-naphthyl) indene; 2-[(4-  
 phenyl)phenyl] indene; and 2-[(3-phenyl) phenyl] indene.

Preferred metallocenes according to the present invention include:

30 bis(2-phenylindenyl) zirconium dichloride;  
 bis(2-phenylindenyl) zirconium dimethyl;



- bis(1-methyl-2-phenylindenyl) zirconium dichloride;  
bis(1-methyl-2-phenylindenyl) zirconium dimethyl;  
bis[2-(3,5-dimethylphenyl)indenyl] zirconium dichloride;  
bis[2-(3,5-bis-trifluoromethylphenyl)indenyl] zirconium dichloride;  
5 bis[2-(3,5-bis-tertbutylphenyl)indenyl] zirconium dichloride;  
bis[2-(3,5-bis-trimethylsilylphenyl)indenyl] zirconium dichloride;  
bis[2-(4,-fluorophenyl)indenyl] zirconium dichloride;  
bis[2-(2,3,4,5,-tetrafluorophenyl)indenyl] zirconium dichloride;  
bis(2-(2,3,4,5,6-pentafluorophenyl)indenyl)) zirconium dichloride;  
10 bis[2-(1-naphthyl)indenyl] zirconium dichloride;  
bis(2-(2-naphthyl)indenyl)) zirconium dichloride;  
bis(2-[(4-phenyl)phenyl]indenyl)) zirconium dichloride;  
bis[2-[(3-phenyl)phenyl]indenyl] zirconium dichloride;  
(pentamethylcyclopentadienyl)(1-methyl-2-phenylindenyl) zirconium dichloride;  
15 (pentamethylcyclopentadienyl)(2-phenylindenyl) zirconium dichloride;  
(pentamethylcyclopentadienyl)(1-methyl-2-phenylindenyl) zirconium dimethyl;  
(pentamethylcyclopentadienyl)(2-phenylindenyl) zirconium dimethyl;  
(cyclopentadienyl)(1-methyl-2-phenylindenyl) zirconium dichloride;  
(cyclopentadienyl)(2-phenylindenyl) zirconium dichloride;  
20 (cyclopentadienyl)(1-methyl-2-phenylindenyl) zirconium dimethyl;  
(cyclopentadienyl)(2-phenylindenyl) zirconium dimethyl;  
(1-methyl-2-phenylindenyl)(2-phenylindenyl) zirconium dichloride;  
(1-methyl-2-phenylindenyl)[2-(3,5-bis-trifluoromethylphenyl)indenyl] zirconium dichloride;  
[1-methyl-2-(3,5-bis-trifluoromethylphenyl)indenyl](2-phenylindenyl) zirconium dichloride;  
25 [1-methyl-2-(3,5-bis-trifluoromethylphenyl)indenyl][2-(3,5-bis-  
trifluoromethylphenyl)indenyl] zirconium dichloride;  
(1-methyl-2-phenylindenyl)[2-(3,5-bis-tertbutylphenyl)indenyl] zirconium dichloride;  
and the corresponding hafnium compounds such as:  
bis(2-phenylindenyl) hafnium dichloride;  
30 bis(2-phenylindenyl) hafnium dimethyl;  
bis(1-methyl-2-phenylindenyl) hafnium dichloride;  
bis(1-methyl-2-phenylindenyl) hafnium dimethyl;  
bis [2-(3,5-dimethylphenyl)indenyl] hafnium dichloride;  
bis[2-(3,5-bis-trifluoromethylphenyl)indenyl] hafnium dichloride;  
35 bis[2-(3,5-bis-tertbutylphenyl)indenyl] hafnium dichloride;  
bis[2-(3,5-bis-trimethylsilylphenyl) indenyl] hafnium dichloride;  
bis[2,(4-fluorophenyl)indenyl] hafnium dichloride;  
bis[2-(2,3,4,5-tetrafluorophenyl)indenyl] hafnium dichloride;

- bis [2-(2,3,4,5,6-pentafluorophenyl)indenyl] hafnium dichloride;  
 bis[2-(1-naphthyl)indenyl] hafnium dichloride;  
 bis[2-(2-naphthyl)indenyl] hafnium dichloride;  
 bis(2-((4-phenyl)phenyl)indenyl)) hafnium dichloride;  
 5 bis[2-[(3-phenyl)phenyl]indenyl] hafnium dichloride;  
 (pentamethylcyclopentadienyl)(1-methyl-2-phenylindenyl) hafnium dichloride;  
 (pentamethylcyclopentadienyl)(2-phenylindenyl) hafnium dichloride;  
 (pentamethylcyclopentadienyl)(1-methyl-2-phenylindenyl) hafnium dimethyl;  
 (pentamethylcyclopentadienyl)(2-phenylindenyl) hafnium dimethyl;  
 10 (cyclopentadienyl)(1-methyl-2-phenylindenyl) hafnium dichloride;  
 (cyclopentadienyl)(2-phenylindenyl) hafnium dichloride;  
 (cyclopentadienyl)(1-methyl-2-phenylindenyl) hafnium dimethyl;  
 (cyclopentadienyl)(2-phenylindenyl) hafnium dimethyl;  
 (1-methyl-2-phenylindenyl)(2-phenylindenyl) hafnium dichloride;  
 15 (1-methyl-2-phenylindenyl)[2-(3,5-bis-trifluoromethylphenyl)indenyl] hafnium dichloride;  
 [1-methyl-2-(3,5-bis-trifluoromethylphenyl)indenyl](2-phenylindenyl) hafnium dichloride;  
 [1-methyl-2-(3,5-bis-trifluoromethylphenyl)indenyl][2-(3,5-bis-  
     trifluoromethylphenyl)indenyl] hafnium dichloride;  
 (1-methyl-2-phenylindenyl)[2-(3,5-bis-tertbutylphenyl)indenyl] hafnium dichloride;  
 20 and the like.

Other metallocene catalyst components of the catalyst system according to the present invention include:

- bis(3,4-dimethyl-1-phenylcyclopentadienyl) zirconium dichloride;  
 bis(3,4-dimethyl-1-p-tolylcyclopentadienyl) zirconium dichloride;  
 25 bis(3,4-dimethyl-1-(3,5 bis(trifluoromethyl)phenyl)cyclopentadienyl)zirconium dichloride;  
 bis(3,4-dimethyl-1-(4-*tert*-butylphenyl)cyclopentadienyl) zirconium dichloride;  
 (3,4-dimethyl-1-phenyl-1,3-cyclopentadiene)(3,4-dimethyl-1-p-tolylcyclopentadienyl)  
     zirconium dichloride;  
 (3,4-dimethyl-1-phenylcyclopentadienyl)(3,4-dimethyl-1-(3,5  
 30 bis(trifluoromethyl)phenyl)cyclopentadienyl) zirconium dichloride;  
 (3,4-dimethyl-1-phenylcyclopentadienyl)(3,4-dimethyl-1-(4-*tert*-butylphenyl)  
     cyclopentadienyl) zirconium dichloride;  
 and the corresponding hafnium compounds, such as:  
 bis(3,4-dimethyl-1-phenylcyclopentadienyl) hafnium dichloride;  
 35 bis(3,4-dimethyl-1-p-tolylcyclopentadienyl) hafnium dichloride;  
 bis(3,4-dimethyl-1-(3,5 bis(trifluoromethyl)phenyl)cyclopentadienyl)hafnium dichloride;  
 bis(3,4-dimethyl-1-(4-*tert*-butylphenyl)cyclopentadienyl) hafnium dichloride;  
 (3,4-dimethyl-1-phenylcyclopentadienyl)(3,4-dimethyl-1-p-tolylcyclopentadienyl)

hafnium dichloride;  
(3,4-dimethyl-1-phenylcyclopentadienyl)(3,4-dimethyl-1-(3,5  
bis(trifluoromethyl)phenyl)cyclopentadienyl) hafnium dichloride;  
(3,4-dimethyl-1-phenylcyclopentadienyl)(3,4-dimethyl-1-(4-*tert*-butylphenyl)  
5 cyclopentadienyl) hafnium dichloride;  
and the like.

It should be understood that other unbridged, rotating, non-rigid, fluxional metallocenes may be employed in the methods of this invention, including those disclosed in our above-identified Provisional application, which is hereby incorporated by reference  
10 to extent needed for support.

The Examples disclose a method for preparing the metallocenes in high yield. Generally, the preparation of the metallocenes consists of forming the indenyl ligand followed by metallation with the metal tetrahalide to form the complex.

Appropriate cocatalysts include alkylaluminum compounds, methylaluminoxane, or  
15 modified methylaluminoxanes of the type described in the following references: U.S. Patent 4,542,199 to Kaminsky, et al.; Ewen, J. Am. Chem. Soc., 106 (1984), p. 6355; Ewen, et al., J. Am. Chem. Soc. 109 (1987) p. 6544; Ewen, et al., J. Am. Chem. Soc. 110 (1988), p. 6255; Kaminsky, et al, Angew. Chem., Int. Ed. Eng. 24 (1985), p. 507. Other cocatalysts which may be used include Lewis or protic acids, such as  $B(C_6F_5)_3$  or  
20  $(PhNMe_2H)^+B(C_6F_5)_4^-$ , which generate cationic metallocenes with compatible non-coordinating anions in the presence or absence of alkyl-aluminum compounds. Catalyst systems employing a cationic Group 4 metallocene and compatible non-coordinating anions are described in European Patent Applications 277,003 and 277,004 filed on 27.01.88 by Turner, et al.; European Patent Application 427,697-A2 filed on 09.10-90 by Ewen, et al.;  
25 Marks, et al., J. Am. Chem. Soc., 113 (1991), p. 3623; Chien, et al., J. Am. Chem. Soc., 113 (1991), p. 8570; Bochmann et al., Angew. Chem. Intl., Ed. Engl. 7 (1990), p. 780; and Teuben et al., Organometallics, 11 (1992), p. 362, and references therein.

The catalysts of the present invention comprise un-bridged, non-rigid, fluxional metallocenes which can change their geometry with a rate that is within several orders of  
30 magnitude of the rate of formation of a single polymer chain, on average. In accordance with the invention, the relative rates of interconversion and of formation can be controlled by selecting the substituents (or absence thereof) of the cyclopentadienyl ligands so that they can alternate in structure between states of different coordination geometries which have different selectivity toward a particular comonomer.

35 In one of many embodiments, these catalyst systems can be placed on a suitable support such as silica, alumina, or other metal oxides,  $MgCl_2$  or other supports. These catalysts can be used in the solution phase, in slurry phase, in the gas phase, or in bulk monomer. Both batch and continuous polymerizations can be carried out. Appropriate

solvents for solution polymerization include liquified monomer, and aliphatic or aromatic solvents such as toluene, benzene, hexane, heptane, diethyl ether, as well as halogenated aliphatic or aromatic solvents such as  $\text{CH}_2\text{Cl}_2$ , chlorobenzene, fluorobenzene, hexafluorobenzene or other suitable solvents. Various agents can be added to control the molecular weight, including hydrogen, silanes and metal alkyls such as diethylzinc.

The metallocenes of the present invention, in the presence of appropriate cocatalysts, are useful for the homo-polymerization and co-polymerization of alpha-olefins, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and combinations thereof, and of copolymerization with ethylene. The polymerization of olefins is carried out by contacting the olefin(s) with the catalyst systems comprising the transition metal component and in the presence of an appropriate cocatalyst, such as an aluminoxane, a Lewis acid such as  $\text{B}(\text{C}_6\text{F}_5)_3$ , or a protic acid in the presence of a non-coordinating counterion such as  $\text{B}(\text{C}_6\text{F}_5)_4^-$ .

The metallocene catalyst systems of the present invention are particularly useful for the polymerization of ethylene and alpha-olefin comonomers as well as alpha-olefin monomer mixtures to produce co-polymers with novel elastomeric properties. The properties of elastomers are characterized by several variables. The tensile set (TS) is the elongation remaining in a polymer sample after it is stretched to an arbitrary elongation (e.g. 100% or 300%) and allowed to recover. Lower set indicates higher elongational recovery. Stress relaxation is measured as the decrease in stress (or force) during a time period (e.g. 30 sec. or 5 min.) that the specimen is held at extension. There are various methods for reporting hysteresis during repeated extensions. In the present application, retained force is measured as the ratio of stress at 50% elongation during the second cycle recovery to the initial stress at 100% elongation during the same cycle. Higher values of retained force and lower values of stress relaxation indicate stronger recovery force. Better general elastomeric recovery properties are indicated by low set, high retained force and low stress relaxation.

### Brief Description of the Drawings

The invention is described, inter alia, with reference to the drawings, in which:

**Fig. 1** is a stereoisomeric representation of unbridged metallocenes of this invention having different substituents in the positions  $\text{R}_1$  through  $\text{R}_{10}$  with the arrows showing the interconversion between states A and B in which the reactivity toward ethylene,  $\text{r}_E$ , and other alpha olefins differs in the two states; and

**Fig. 2** shows four possible coordination geometries for unbridged metallocenes of this invention, with the circles representing coordination sites for olefin insertion.



### Detailed Description Including The Best Mode of Carrying Out The Invention

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives and uses of the invention, including what are presently  
5 believed to be the best modes of carrying out the inventions.

In this regard, the invention is illustrated in the several examples, and is of sufficient complexity that the many aspects, interrelationships, and sub-combinations thereof simply cannot be fully illustrated in a single example. For clarity and conciseness,  
10 several of the examples show, or report only aspects of a particular feature or principle of the invention, while omitting those that are not essential to or illustrative of that aspect. Thus, the best mode embodiment of one aspect or feature may be shown in one example or test, and the best mode of a different aspect will be called out in one or more other examples, tests, structures, formulas, or discussions.

The metallocene catalysts of the present invention are represented in one embodiment in Figure 1 where the ligands L and L' are substituted cyclopentadienyl rings. As shown in the Figure, in state A cyclopentadienyl substituents R<sub>1</sub>, R<sub>2</sub> and R<sub>6</sub> and R<sub>7</sub> project over the ligands X = X' whereas in state B, cyclopentadienyl substituents R<sub>1</sub>, R<sub>2</sub> and R<sub>8</sub> and R<sub>9</sub> project over the ligands X = X'. As provided for in the process of this  
15 invention, catalysts derived from these metallocenes where substituents R<sub>6</sub> and R<sub>7</sub> are different from R<sub>8</sub> and R<sub>9</sub> will exhibit reactivity ratios for ethylene in state A (r<sub>EA</sub>) different from that in state B (r<sub>EB</sub>).  
20

Another embodiment of the invention is illustrated in Figure 2 where the ligands L and L' are different substituted 2-arylindenyl ligands such that the metallocene interconverts between four states with different coordination geometries. As shown in the  
25 Figure, in two states a methyl group projects over the coordination sites for olefin insertion (represented in this figure by circles) and in two states the methyl group projects away from the coordination sites for the olefin. The following examples illustrate the control of the polymer properties via selection of the ligand substitution groups.

30

### EXAMPLES.

All organometallic reactions were conducted using standard Schlenk and drybox techniques. Elemental analyses were conducted by E+R Microanalytical Laboratory. Unless otherwise specified all reagents were purchased from commercial suppliers and used  
35 without further purification. 2-Phenylindene, 1-methyl-2-phenylindene, 2-(bis(3',5'-trifluoromethyl) phenylindene, bis(2-phenylindenyl)zirconium dichloride, *rac*- and *meso*-bis(1-methyl-2-phenylindenyl)zirconium dichloride, ethylene-bis(indenyl)zirconium dichloride and bis(2-(bis(3',5'-trifluoromethyl)phenylindenyl)-zirconium dichloride were



prepared according to the literature procedures. (Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1-6.) Hexane, pentane and methylene chloride used in organometallic synthesis were distilled from calcium hydride under nitrogen. Tetrahydrofuran was distilled from sodium/benzophenone under nitrogen. Toluene, ethylene and propylene were passed through two purification columns packed with activated alumina and supported copper catalyst. 1-Hexene and chloroform-*d*<sub>3</sub> were distilled from calcium hydride and benzene-*d*<sub>6</sub> was distilled from sodium/benzophenone.

### I. Metallocene Synthesis

**Ethylene-bis(indenyl)zirconium dichloride (Metallocene 1).** This complex was prepared as described in Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63-7.

**Bis(2-phenylindenyl)zirconium dichloride (Metallocene 2).** This complex was prepared as described in Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174-11182.

**Bis(2-phenylindenyl)hafnium dichloride (Metallocene 3).** This complex was prepared as described in Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174-11182.

#### Example 1. Preparation of 2-(bis-3,5-trifluoromethylphenyl)indene (Ligand A)

A 3-neck 500 mL round-bottomed flask fitted with a condenser and an addition funnel was charged with 2.62g (0.11 mol) of Mg turnings and 20 mL of anhydrous diethyl ether. Slow addition of a solution of 25.10 g (0.09 mol) of 3,5-bis(trifluoromethyl) bromobenzene in diethyl ether (100 mL), followed by refluxing for 30 min, gave a brown-grey solution of the aryl Grignard reagent. The solution was cooled to room temperature (RT), filtered over a plug of Celite and evacuated to yield a brown oil. Toluene (40 mL) was added and the suspension cooled to 0°C whereupon a solution of 2-indanone (9.22 g, 0.07 mol) in toluene (60 mL) was added dropwise to give a tan-brown slurry. This mixture was warmed to room temperature and stirred for an additional 3 hours. After cooling to 0°C it was quenched with 150 mL of water, hexane (200 mL) added and the reaction mixture neutralized with 5M HCl. The organic layer was separated, and the aqueous layer was extracted with two 50-mL portions of hexane. The combined organic layers were washed with two 50-mL portions of brine and dried over anhydrous magnesium sulfate. After filtration over Celite, the solvent was removed under vacuo yielding 21.5 g (89% based on 2-indanone) of 2-(bis-3,5-trifluoromethylphenyl) indanol as an off-white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 23 °C, 400 MHz): δ 8.05 (s, 2H), 7.80 (s, 1H), 7.5-7.0 (M,

4H), 3.41 (m, 4H), 2.21 (s, 1H, OH). Under argon, this alcohol (21.5 g, 0.06 mol) and p-toluene-sulfonic acid monohydrate (800 mg) were dissolved in toluene (250 mL) and the solution was heated to reflux for 6 hours to afford 14.4 g, (70%) of 2-(bis-3,5-(trifluoromethyl)-phenyl) indene upon recrystallization from diethyl ether/hexane at -18 C.

5  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 23°C, 400 MHz): d 8.01 (s, 2H, Arf), 7.75 (s, 1H, Arf), 7.52 (d, J = 7 Hz, 1H), 7.47 (d, J = 7 Hz, 1H), 7.43 (s, 1H), 7.33 (dd, 2J = 7 Hz, 1H), 7.27 (dd, 2J=7 Hz, 1H), 2.83 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 23 C, 100 MHz): L144.3 (s), 143.1 (s), 138.0 (s), 132.1 (q,  $^2\text{J}_{\text{C-F}}$  = 33 Hz), 130.1 (d,  $\text{J}_{\text{C-H}}$  = 167 Hz), 127.0 (dd,  $\text{J}_{\text{C-H}}$  = 160 Hz,  $^2\text{J}_{\text{C-H}}$  = 7 Hz), 126.0 (dd,  $\text{J}_{\text{C-H}}$  = 159 Hz,  $^2\text{J}_{\text{C-H}}$  = 7 Hz)m 125.2 (brd,  $\text{J}_{\text{C-H}}$  = 162 Hz), 123.9 (dd,  $\text{J}_{\text{C-H}}$  = 156 Hz,  $^2\text{J}_{\text{C-H}}$  = 9 Hz), 123.4 (q,  $\text{J}_{\text{C-F}}$  = 273 Hz,  $\text{CF}_3$ ), 121.8 (dd,  $\text{J}_{\text{C-H}}$  = 160 Hz,  $^2\text{J}_{\text{C-H}}$  = 8 Hz), 120.6 (brd,  $\text{J}_{\text{C-H}}$  = 167 Hz), 38.9 (td,  $\text{J}_{\text{C-H}}$  = 127 Hz,  $^2\text{J}_{\text{C-H}}$  = 7 Hz,  $\text{CH}_2$ ). C,H analysis: Anal. Found (Calcd): C, 62.45 (62-20); H 3.01 (3.07).

15 **Example 2. Preparation of Bis(2-(bis-3,5-trifluoromethylphenyl)indenyl) zirconium dichloride, (Metallocene 4)**

N-Butyllithium (2.5 M in hexanes, 0.850 mL, 2.13 mmol) was added to a solution of 2-(bis-3,5-trifluoromethylphenyl) indene (648 mg, 1.97 mmol) in toluene (15 mL). The heterogeneous solution was stirred at ambient temperature for 4 hours 30 minutes to give a

20 green-yellow solution which was treated with a suspension of  $\text{ZrCl}_4$  (240 mg, 1.03 mmol) in toluene (20 mL) via cannula. The yellow suspension was stirred at room temperature for 2.5 hours, heated to ca. 80° C, and filtered over a plug of Celite. After washing the Celite with hot toluene several times (3 x 10 mL), the filtrate was concentrated and cooled to 18 C to give 442 mg (55%) of light yellow crystals of Bis(2-(Bis-3,5-trifluoromethylphenyl)-indenyl)zirconium dichloride.

25  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 C, 400 MHz): d 7.67 (s, 2H, Arf), 7.55 (s, 4H, Arf), 7.19 (m, 4H, Ar), 6.89 (m, 4H, Ar), 5.96 (s, 4H, Cp-H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 23 C, 100 MHz: d 135.6 (s), 133.1 (s), 131.6 (q,  $^2\text{J}_{\text{C-F}}$  = 33 Hz), 127.1 (brd,  $\text{J}_{\text{C-H}}$  = 161 Hz), 126.8 (s), 126.4 (dd,  $\text{J}_{\text{C-H}}$  = 161 Hz,  $^2\text{J}_{\text{C-H}}$  = 8 Hz), 125.4 (dd,  $\text{J}_{\text{C-H}}$  = 167 Hz,  $^2\text{J}_{\text{C-H}}$  = 5 Hz), 123.8 (q,  $\text{J}_{\text{C-F}}$  = 273 Hz,  $\text{C-F}$ ), 121.8 (brd,  $\text{J}_{\text{C-H}}$  = 159 Hz), 102.5 (dd,  $\text{J}_{\text{C-H}}$  = 176 Hz,  $^2\text{J}_{\text{C-H}}$  = 7 Hz, Cp ( $\text{C-H}$ )). C,H analysis: Anal. found (Calcd.): C, 49.99 (50.01); H 2.32 (2.22).

30

**Example 3. Preparation of Bis(2-(bis-3,5-trifluoromethylphenyl)indenyl) hafnium dichloride, (Metallocene 5)**

35 N-Butyllithium (1.6M in hexanes, 2 mL, 3.20 mmol) was added dropwise at room temperature to a solution of 2-(bis-3,5-trifluoromethylphenyl)indene (1.03 g, 3.14 mmol) in diethyl ether (10 mL). After stirring for 30 min, the solvent was removed *in vacuo* leaving a green-yellow solid. In a drybox,  $\text{HfCl}_4$ , (510 mg, 1.59 mmol) was added to the

lithium salt. The solids were then cooled to -78 °C at which temperature toluene (45 mL) was slowly added. The flask was allowed to reach ambient temperature and the suspension was stirred for 24 hours after which time it was heated for 15 min to ca. 80 °C (heat gun). The solvent was then removed *in vacuo*. The solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the solution filtered over a plug of Celite. After washing the Celite with 4 x 15 mL CH<sub>2</sub>Cl<sub>2</sub>, the solvent was removed *in vacuo* from the filtrate. The solid was dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered and over filtrate a layer of hexane (40 mL) was slowly added. Crystals of Bis(2-(bis-3,5-trifluoromethylphenyl)indenyl) hafnium dichloride Catalyst E were obtained from this layered solution at -18 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 23 °C, 200 MHz): d 7.65 (s, 2H, Arf), 7.51 (s, 4H, Arf), 6.7-7.3 (m, 8H Ar), 5.63 (s, 4H, Cp-H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub> 23 °C, 100 MHz): d 135.8 (s), 132.9 (s), 131.6 (q, <sup>2</sup>J<sub>C-F</sub> = 34 Hz), 127.2 (brd, J<sub>C-H</sub> = 160 Hz), 126.3 (dd, J<sub>C-H</sub> = 161 Hz, <sup>2</sup>J<sub>C-H</sub> = 8 Hz), 126.0 (s), 125.6 (dd, J<sub>C-H</sub> = 167 Hz, <sup>2</sup>J<sub>C-H</sub> = 5 Hz), 123.8 (q, J<sub>C-F</sub> = 273 Hz, C<sub>CF3</sub>), 121.7 (brd, J<sub>C-H</sub> = 161 Hz), 100.1 (dd, J<sub>C-H</sub> = 176 Hz, <sup>2</sup>J<sub>C-H</sub> = 6 Hz, Cp C-H). C, H analysis: Anal. Found (Calcd.): C, 45.10 (45-18); H, 1.87 (2.01).

**Example 4. 1-Methyl-2-(bis-3',5'-trifluoromethylphenyl)indene and 3-methyl-2-(bis-3',5'-trifluoromethylphenyl)indene.**

A solution of 2-bis-3',5'-trifluoromethylphenyl)indene (1.819 g, 5.54 mmol) in tetrahydrofuran (30 mL) was cooled to -78 °C and BuLi (2.5 M in hexanes, 2.33 mL, 5.82 mmol) was added dropwise. The resulting orange-brown solution was allowed to warm to room temperature and stirred for an additional 30 min. Then CH<sub>3</sub>I (1.20 mL, 19 mmol) was added to this solution and the greenish reaction mixture was stirred for 20 h at room temperature. Methanol (20 mL) was added and the solvents removed *in vacuo*. The resulting brown solid was extracted with toluene (30 mL) and filtered through a glass frit packed with Celite. The brown solution was washed with H<sub>2</sub>O (2 x 10 mL) and saturated NaCl solution (2 x 10 mL), dried over MgSO<sub>4</sub>, and then evaporated to dryness. Crystallization from hexanes gave yellow crystals of 5.7 (1.073 g). <sup>1</sup>H NMR (20 °C, CDCl<sub>3</sub>, 400 MHz): 7.87 (s, 2H), 7.75 (s, 1H), 7.49 (d, 1H, J = 7.3 Hz), 7.42 (d, 1H, J = 7.6 Hz), 7.37 (t, 1H, J = 7.3 Hz), 7.26 (td, 1H, J = 7.3 Hz, J = 1.2 Hz), 3.78 (s, 2H), 2.33 (s, 3H). Anal. Calcd (Found) for C<sub>18</sub>H<sub>12</sub>F<sub>6</sub>: C, 63.16 (63.12); H 3.53 (3.62). Repeated crystallization from hexanes gave a mixture of isomers of the ligand (309 mg) in 4 : 1 ratio. <sup>1</sup>H NMR: 3.14 (q, 1H, J = 7.0 Hz), 0.87 (d, 3 H, J = 7.1 Hz). Overall yield 1.073 g, 73%.

**Example 5. Synthesis of (2-phenylindenyl) zirconium trichloride.**

Solid Zr(NMe<sub>2</sub>)<sub>4</sub> (1.280 g, 4.785 mmol) and 2-phenylindene (0.920 g, 4.785 mmol) were combined with toluene (30 mL) in a 100-mL Schlenk tube and the resulting

pale yellow solution was stirred for 2.5 h at room temperature under slightly reduced pressure. Then the solution was evaporated to dryness to give a yellow oil which was extracted with pentane (20 mL) and filtered through a *cannula* fitted with a double layer of filter paper. The resulting pentane solution was concentrated to a total volume of 10 mL and placed into a -50 °C freezer overnight. The resulting yellow solid was isolated, dried in *vacuo*, and redissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The pale yellow solution was cooled to 0 °C and chlorotrimethylsilane (2 mL, 15.8 mmol) was added *via* syringe. The bright yellow solution was allowed to warm to room temperature and stirred for 1 h. Then the solution was evaporated to dryness to yield a yellow/orange foamy solid. Toluene (30 mL) was added and the mixture was stirred for 48 h to yield a lemon yellow powder, which was isolated and dried *in vacuo* (1.098 g, 59% yield). This material was used without further purification.

**Example 6. Synthesis of (2-phenylindenyl)(1-methyl-2-phenylindenyl) zirconium dichloride, (Metallocene 6).**

Butyllithium (2.5 M in hexane, 0.43 mL, 1.08 mmol) was added *via* syringe to the solution of 1-methyl-2-phenylindenyl (212 mg, 1.029 mmol) in diethyl ether (25 mL) at -78 °C. The resulting light yellow solution was allowed to warm to room temperature and stirred for additional 30 min. The ether was removed *in vacuo* to yield a white powdery solid, which was combined with solid (2-phenylindenyl)zirconium trichloride (400 mg, 1.029 mmol) and toluene (50 mL). The resulting suspension was stirred for 24 h at room temperature. Gradually the solids dissolved to give a yellow turbid solution. The mixture was filtered through a glass frit packed with Celite and then evaporated to dryness. The resulting yellow solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (10 mL) layered with pentane (30 mL) at -50 °C to give metallocene 6., 181 mg, 31 % yield. <sup>1</sup>H NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 400 MHz): d 7.41 (d, 2H, *J* = 11.2 Hz), 7.30 (d, 2H, *J* = 10.8 Hz), 7.24-6.80 (m, 13H), 6.73 (d, 1H, *J* = 11.2 Hz), 6.50 (d, 1H, *J* = 3.2 Hz), 6.26 (d, 1H, *J* = 3.3 Hz), 5.98 (s, 1H), 2.42 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (20 °C, CDCl<sub>3</sub>, 125 MHz): d 133.75 (C), 133.10 (C), 132.38 (C), 131.41 (C), 129.54 (C), 129.06 (C-H), 128.90 (C-H), 128.70 (C-H), 128.67 (C-H), 128.14 (C-H), 126.95 (C), 126.72 (C-H), 126.58 (C-H), 126.56 (C-H), 126.43 (C-H), 126.26 (C-H), 125.58 (C-H), 125.05 (C), 124.90 (CH), 124.56 (C), 124.35 (C-H), 123.68 (C-H), 121.43 (C), 104.34 (C-H, Cp), 100.70 (C-H, Cp), 99.00 (C-H, Cp), 12.54 (CH<sub>3</sub>). Anal. Calcd (Found) for C<sub>31</sub>H<sub>24</sub>Cl<sub>2</sub>Zr: C 66.65 (66.92); H 4.33 (4.36).

**Example 7. Synthesis of (2-phenylindenyl)(1-methyl-2-(bis-3', 5'-trifluoromethylphenyl)indenyl) zirconium dichloride, Metallocene 7.**



Butyllithium (2.5 M in hexanes, 0.43 mL, 1.08 mmol) was added to the pale yellow solution of 1-methyl-2-(bis-3',5'-trifluoromethylphenyl)indene (352 mg, 1.029 mmol) in diethyl ether (20 mL) at -78 °C *via* syringe. The resulting yellow solution was allowed to warm to room temperature and stirred for additional 30 min. Ether was removed *in vacuo* to yield a pale yellow solid which was washed with pentane (20 mL) and combined with solid (2-phenylindenyl)zirconium trichloride (400 mg, 1.029 mmol) and toluene (50 mL). The resulting suspension was stirred for 24 h at room temperature. Gradually the solids dissolved to give a yellow turbid solution. This solution was filtered through a glass frit packed with Celite and then evaporated to dryness. The yellow solid **7** was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (10 mL) layered with pentane (20 mL) at -50 °C: (245 mg, 34 %). <sup>1</sup>H NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 400 MHz): 7.67 (s, br, 1H), 7.64 (s, br, 2H), 7.30-6.78 (m, 13H), 6.43 (d, 1H, *J* = 2.4 Hz), 6.19 (d, 1H, *J* = 2.4 Hz), 5.59 (s, 1H), 5.32 (s, 1/3 H, CH<sub>2</sub>Cl<sub>2</sub>), 2.24 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (20 °C, CDCl<sub>3</sub>, 125 MHz): 135.91 (C-H), 133.59 (C), 132.58 (C), 131.47 (C-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 33 Hz), 130.76 (C), 130.51 (C), 129.02 (C-H), 128.98 (C-H), 128.80 (C-H), 126.87 (C-H), 126.81 (C-H), 126.77 (C-H), 126.62 (C-H), 126.52 (C-H), 126.25 (C-H), 126.21 (C), 125.34 (C-H), 125.05 (C), 124.09 (C-H), 123.86 (C), 123.23 (CF<sub>3</sub>, *J*<sub>CF</sub> = 273 Hz), 123.17 (C), 121.24 (C-H, br), 119.25 (C), 102.70 (C-H, Cp), 101.76 (C-H, Cp), 99.30 (C-H, Cp), 12.12 (CH<sub>3</sub>). Anal. Calcd (Found) for C<sub>33</sub>H<sub>22</sub>Cl<sub>2</sub>F<sub>6</sub>Zr x 1/6·CH<sub>2</sub>Cl<sub>2</sub>: C 55.86 (56.20); H 3.37 (3.18). After having been stored for 3-4 weeks in the drybox in a clear vial the yellow compound turned green in color. No changes in <sup>1</sup>H NMR spectrum were detected upon the color change.

**Example 8. Synthesis of (2-(bis-3',5'-trifluoromethylphenyl)indenyl) zirconium trichloride.**

Solid Zr(NMe<sub>2</sub>)<sub>4</sub> (1.260 g, 4.713 mmol) and 1-methyl-2-(bis-3',5'-trifluoromethylphenyl)indene (1.505 g, 4.58 mmol) were combined with toluene (30 mL) in a 100-mL Schlenk tube and the resulting greenish-brown solution was stirred for 2.5 h at room temperature under slightly reduced pressure. Then the solution was evaporated to dryness to give greenish-brown solid, which was extracted with pentane (30 mL) and filtered through a *cannula* fitted with a double layer of filter paper. The resulting pentane solution was concentrated to a total volume of 8 mL and placed in a -50 °C freezer overnight. Greenish-brown crystals formed. They were isolated, dried *in vacuo* and redissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The resulting solution was cooled to 0 °C and chlorotrimethylsilane (2 mL, 15.8 mmol) was added *via* syringe. The turbid yellow solution was allowed to warm to room temperature, stirred for 1 h, concentrated to a total volume of 1 mL and then diluted with toluene (30 mL). The resulting suspension was stirred for 24 h. The lemon yellow powdery solid was isolated and dried *in vacuo* (1.390 g, 46 %). <sup>1</sup>H NMR (20 °C, CDCl<sub>3</sub>, 400 MHz): 8.19-8.17 (br, 1H), 8.10 (br, 2H), 7.99



(br, 1H), 7.83 (br, 1H), 7.77 (br, 1H), 7.61 (br, 2H), 7.53 (appears as poorly resolved dd, 2H), 7.44-7.38 (br, 1H), 7.30 (br, 2H), 7.20 (m, 1H), 7.03 (br, 2H), 6.95 (s, 1H), 6.83 (br, 1H), 2.45 (br, 6H), 0.41 (s, 9H). Broad peaks in the aromatic region appear to indicate the presence of dimerized or oligomerized forms of (bfmPhIn)ZrCl<sub>3</sub>. In addition, one NMe<sub>2</sub> group (2.45 ppm) and one SiMe<sub>3</sub> group (0.41 ppm) per every two 2-bis(3',5'-trifluoromethyl)-phenylindenyl entities appear to be coordinated to the metal. This material was used without further purification.

**Example 9. Synthesis of (2-(bis-3',5'-trifluoromethylphenyl)indenyl)(1-methyl-2-phenylindenyl) zirconium dichloride, (Metallocene 8).**

Butyllithium (2.5 M in hexanes, 0.55 mL, 1.38 mmol) was added to the solution of 1-methyl-2-phenylindene (277 mg, 1.31 mmol) in diethyl ether (25 mL) at -78 °C *via* syringe. The resulting light yellow solution was allowed to warm to room temperature, stirred for an additional 15 min, and the ether was removed *in vacuo* to yield a white powdery solid which was combined with solid (2-(bis-3',5'-trifluoromethylphenyl)indenyl) zirconium trichloride·Me<sub>3</sub>SiNMe<sub>2</sub> (695 mg, 1.31 mmol) and toluene (40 mL) at 0 °C. The resulting dark green solution was allowed to warm to room temperature and stirred for 40 h during which time the color of the solution gradually turned lemon-yellow. The turbid solution was filtered through a glass frit packed with Celite and then evaporated to dryness. Orange crystals were obtained from a CH<sub>2</sub>Cl<sub>2</sub> (5 mL)/pentane (5 mL) solution stored at -50 °C (200 mg, 28 %). <sup>1</sup>H NMR (20 °C, CDCl<sub>3</sub>, 500 MHz): d 7.84 (s, 2H, br), 7.82 (s, 1H, br), 7.52 (t, 2H, *J* = 7.5 Hz), 7.43 (m, 3H), 7.36 (m, 2H), 7.29 (m, 2H), 7.20 (t, 1H, *J* = 6.0 Hz), 7.08 (q, 2H, *J* = 7.0 Hz), 6.68 (d, 1H, *J* = 2 Hz), 6.38 (d, 1H, *J* = 2 Hz), 5.99 (s, 1H), 5.32 (s, 1/3 H, CH<sub>2</sub>Cl<sub>2</sub>), 2.53 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (20 °C, CDCl<sub>3</sub>, 125 MHz): d 135.48 (C), 133.20 (C), 132.23 (C), 132.20 (C), 131.62 (C-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 34 Hz), 130.23 (C), 129.03 (CH), 128.61 (CH), 128.44 (C-H), 126.87 (C-H), 126.71 (C-H), 126.70 (C-H), 126.54 (C-H), 126.45 (C-H), 126.24 (C-H), 125.90 (C), 125.17 (C-H), 125.01 (C), 124.43 (C), 124.15 (C-H), 124.13 (C-H), 123.22 (CF<sub>3</sub>, *J*<sub>C-F</sub> = 272 Hz), 121.70 (C-H, br), 102.09 (C-H, Cp), 101.20 (C-H, Cp), 98.51 (C-H, Cp), 12.39 (CH<sub>3</sub>). Anal. Calcd (Found) for C<sub>33</sub>H<sub>22</sub>Cl<sub>2</sub>F<sub>6</sub>Zr x 1/6·CH<sub>2</sub>Cl<sub>2</sub>: C 56.20 (56.11); H 3.18 (3.09).

**Example 10. Synthesis of (2-(bis-3',5'-trifluoromethylphenyl)indenyl)(1-methyl-2-(bis-3',5'-trifluoromethylphenyl)indenyl) zirconium dichloride, (Metallocene 9).**

Butyllithium (2.5 M in hexanes, 0.40 mL, 1.00 mmol) was added to the solution of 2-(bis-3,5-trifluoromethylphenyl)indene (328 mg, 0.958 mmol) in diethyl ether (30 mL) at -78 °C *via* syringe. The resulting light yellow solution was allowed to warm to room

temperature, stirred for additional 2.5 h and the ether was removed *in vacuo* to yield a gray powdery solid, which was washed with pentane, filtered, and dried *in vacuo*. The solid was then combined with solid (2-(bis-3',5'-trifluoromethylphenyl)indenyl) zirconium trichloride·Me<sub>3</sub>SiNMe<sub>2</sub> (508 mg, 0.958 mmol) and toluene (50 mL) and the reaction mixture was stirred for 40 h at room temperature. The turbid yellow solution was filtered through a glass frit packed with Celite and then evaporated to dryness. The resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The yellow methylene chloride solution was placed in a -50 °C freezer overnight and a yellow precipitate formed (100 mg, 13 %). <sup>1</sup>H NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 500 MHz): d 7.56 (s, 2H, br), 7.48 (s, 2H, br), 7.29 (d, 1H, *J* = 8.5 Hz), 7.08 (m, 2H), 6.90 (m, 2H), 6.83 (t, 2H, *J* = 7.0 Hz), 6.66 (t, 1H, *J* = 7.5 Hz), 6.00 (d, 1H, *J* = 2.5 Hz), 5.73 (d, 1H, *J* = 2.5 Hz), 5.48 (s, 1H), 2.14 (s, 3H). <sup>19</sup>F NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 282 MHz): 63.65 (s, 3F), 63.57 (s, 3F). <sup>13</sup>C {<sup>1</sup>H} NMR (20°C, CDCl<sub>3</sub>, 125 MHz): d 135.61 (C), 133.85 (C), 132.66 (C), 131.64 (C-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 33 Hz), 131.44 (C-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 33 Hz), 130.78 (C), 129.03 (CH), 129.00 (CH), 127.85 (C), 126.79 (CH), 126.63 (CH), 126.57 (CH), 126.35 (CH), 125.91 (CH), 124.95 (CH), 124.74 (C), 124.59 (CH), 124.28 (CH), 123.50 (CF<sub>3</sub>, *J*<sub>C-F</sub> = 273 Hz), 123.15 (CF<sub>3</sub>, *J*<sub>C-F</sub> = 273 Hz), 122.83 (C), 122.09 (C), 121.89 (CH, br), 121.42 (CH, br), 118.74 (C), 103.28 (CH, Cp), 100.28 (CH, Cp), 99.57 (CH, Cp), 12.17 (CH<sub>3</sub>). Anal. Calcd (Found) for C<sub>35</sub>H<sub>20</sub>Cl<sub>2</sub>F<sub>12</sub>Zr: C 50.61 (50.90); H 2.43 (2.72).

**Example 11. Synthesis of Bis(2-(bis-3,5-*tert*-butyl-4-methoxyphenyl)indenyl) zirconium dichloride (Metallocene 10).**

A sample of 5.584 g (40 mmol) potassium carbonate and 6.3 mL (100 mmol) iodomethane were reacted with 2.554 g (10 mmol) bis-3,5-*tert*-butyl-4-hydroxybenzoic acid and heated to 45 °C for 30 h. Flash chromatography of the crude product on silica gel with 7.5% ether in hexanes then recrystallisation from hexanes at -20 °C yielded methyl-bis-3,5-*tert*-butyl-4-methoxybenzoate. Yield: 2.213 g (7.95 mmol, 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): d 1.42 (s, 18H), 3.68 (s, 3H), 3.87 (s, 3H), 7.93 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): d 31.91, 35.86, 51.93, 64.40, 124.35, 128.24, 144.01, 163.84, 167.45. The methyl ester (8 mmol) was dissolved in 65 mL of THF in an addition funnel and added to a solution of the di-Grignard of o-xylylenedichloride solution at -78 °C over approx. 60 minutes, consistently maintaining the temperature below -70 °C during the addition. The reaction mixture was warmed to 0 °C in 1-2 h and 80 mL distilled water was added through the addition funnel in 15-30 minutes. After the reaction mixture was allowed to warm to room temperature the THF was removed completely from the reaction mixture. The remaining suspension was acidified to pH=1 and extracted with methylene chloride. The combined organic layers were dried over magnesium sulfate and stirred with 0.300 g (1.57 mmol) *para*-toluenesulfonic acid monohydrate for 1 h at room temperature. After extraction with

distilled water and drying over magnesium sulfate, the crude product was transferred to silica gel and purified by flash chromatography. Yield 2.346 g (7.01 mmol, 87%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): d 1.47 (s, 18H), 3.71 (s, 3H), 3.79 (s, 2H), 7.14 (s, 1H), 7.15 (td,  $J = 7.0$  Hz,  $J = 0.8$  Hz), 1H), 7.25 (t,  $J = 7.5$  Hz, 1H), 7.37 (d,  $J = 7.5$  Hz, 1H), 7.62 (d,  $J = 7.5$  Hz, 1H), 7.54 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): d 32.18, 36.09, 39.47, 64.65, 120.88, 123.89, 124.41, 124.68, 125.36, 126.87, 130.67, 143.53, 144.24, 146.05, 147.55, 159.94.

A sample of 1.5 mmol of 2-(bis-3,5-*tert*-butyl-4-methoxyphenyl)indene was dissolved in 50 mL of diethylether. The solution was cooled down to 0 °C and 0.6 mL (1.5 mmol) *n*-butyllithium (2.5 M in hexanes) was added dropwise via syringe. The cooling bath was removed and the mixture was stirred at ambient temperature for 10 h and evacuated to dryness. Zirconium tetrachloride, 175 mg (0.75 mmol), and 100 mL toluene was added and the reaction mixture stirred vigorously at 25°C for 3 days. Toluene was removed *in vacuo* and 50 mL methylene chloride added. The suspension was filtered over celite through a Schlenk-frit under argon and washed with methylene chloride until the filtered liquid remained colorless. The resulting clear solution's volume was reduced to 1/4 to 1/5 and a layer of pentane, hexanes or diethylether was applied carefully. The layered solution was stored at -80 °C for crystallization of the product. Yield: 293 mg (0.353 mmol, 36%), yellow solid.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): d 1.56 (s, 36H), 3.82 (s, 6H), , 6.64-6.68 (m, 4H), 6.72 (s, 4H), 6.98-7.01 (m, 4H), 7.63 (s, 4H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): d 32.16, 36.13, 64.67, 104.50, 124.32, 125.48, 126.11, 126.40, 127.03, 129.51, 144.65, 160.45. Anal. Calcd for  $\text{C}_{48}\text{H}_{58}\text{Cl}_2\text{O}_2\text{Zr}$ : C, 69.54; H, 7.05. Found: C, 69.41; H, 7.24.

### General Polymerization Procedures:

#### METHOD A. Copolymerization of Ethylene and Propylene (< 50 mole % E).

A 300-mL stainless steel Parr reactor was charged with liquid propylene (100 mL). Propylene was cooled to the reaction temperature and pressurized with ethylene. The monomer mixture was equilibrated at the reaction temperature under constant ethylene pressure for at least 20 min. Immediately prior to the catalyst injection the ethylene line was disconnected and the reactor was cooled to 2-3 °C below the reaction temperature to compensate for the anticipated exothermic effect of catalyst injection. In a nitrogen filled drybox a 50-mL pressure tube was charged with zirconocene/MAO solution in toluene (20 mL), removed from the box and pressurized with argon (250 psig). In the case of polymerizations at 0-2 °C the catalyst injection tube was cooled in an ice bath prior to being injected. The reaction was started by catalyst injection. After catalyst injection, the ethylene line was reconnected and the reaction was run for 15-60 min at constant total pressure and temperature. The reaction was quenched by injecting MeOH (20 mL). The

polymer was precipitated in acidified MeOH (5% HCl), filtered, washed with MeOH and dried in a vacuum oven at 40 °C to constant weight.

#### **METHOD B. Copolymerization of Ethylene and Propylene (> 60 mole % E).**

5           A 300-mL Parr autoclave was charged with 60 mL of liquid propylene and cooled to the reaction temperature. MAO, dissolved in 10 mL of toluene, was injected under ethylene pressure and the reactor was allowed to equilibrate for 10-15 min. Polymerization was initiated by injecting the corresponding zirconocene dichloride solution in 10 mL of toluene under ethylene pressure set to 30-40 psi above the head pressure of preequilibrated  
10 ethylene/propylene mixture in the reactor. Polymerization was conducted for 25 min and quenched by injecting 10 mL of methanol under Ar pressure. The reactor was slowly vented and opened. The copolymer was precipitated in acidified methanol (5% HCl), filtered, washed with methanol and dried in a vacuum oven at 40 °C to constant weight.

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#### **METHOD C. Ethylene-Hexene Copolymerization.**

The metallocene was dissolved in 25 mL of toluene in the N<sub>2</sub> dry box. Methylaluminoxane (MAO) was dissolved in 35 mL of 1-hexene. The MAO solution was loaded into a 150 mL 2-ended injection tube. Meanwhile, a 300 mL stainless steel Parr  
20 reactor was evacuated to 100 mtorr and refilled with Ar. The reactor was flushed three times with 50 psig Ar and then 129 psig ethylene. The MAO solution was introduced to the reactor and was allowed to equilibrate with under the desired head pressure of ethylene for 30 min. 1-Hexene (3.2 mL) and an aliquot of metallocene stock solution (1.8 mL) was introduced to a 25 mL 2-ended injection tube. The ethylene feed was disconnected from  
25 the reactor and the pressure was vented by 10 psig. The metallocene solution was injected under the desired head pressure of ethylene to start the reaction. The ethylene feed was immediately reconnected to the reactor. The temperature was controlled at 18 °C throughout the reaction via an ethylene glycol/water cooling loop. The reaction was quenched with methanol injected under Ar pressure after 1 h. The reactor was vented and  
30 the copolymer was collected and stirred with acidified methanol overnight. The copolymer was then rinsed with methanol and dried to constant weight in a vacuum oven at 40 °C.

#### **METHOD D. Ethylene Homopolymerization.**

35           The homopolymerization procedure was identical to that employed in copolymerizations. However, hexane was substituted for 1-hexene as the reaction solvent.

#### **Ethylene-Propylene Copolymer Characterization.**



Copolymer composition and monomer sequence distribution were determined using  $^{13}\text{C}$  NMR spectroscopy. Copolymer samples (180-300 mg) were dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol. % benzene- $d_6$  in 10 mm tubes. The spectra were measured at 140 °C using pulse repetition intervals of 13 s and gated proton decoupling. The isotacticity of propylene triads (%*mm*) was determined from the ratio of integrals of the first triplet in the methyl region (all PMPMP centered triads) over  $T_{\beta\beta}$  peak (all PPP triads). The glass transition, melting points and heats of fusion were determined by differential scanning calorimetry using Perkin-Elmer DSC-7. The DSC scans were obtained by first heating copolymer samples to 160 °C for 20 min, cooling them to 20 °C over 2 h, ageing them at room temperature for 24 h and then reheating from -100 °C to 200 °C at 20 °C/min. All DSC values in the tables are reheat values. Infrared spectra were obtained by transmission on melt-pressed films using a Perkin-Elmer 1600 FTIR spectrometer. The IR ratio =  $A_{993}/A_{975}$ , calculated from the absorptivities at 993 and 975  $\text{cm}^{-1}$ , was averaged over at least three measurements taken in different regions of the film.

#### Ethylene-1-Hexene Copolymer Characterization.

Copolymer composition and monomer sequence distribution were determined using  $^{13}\text{C}$  NMR spectroscopy. Copolymer samples (180-300 mg) were dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol. % benzene- $d_6$  in 10 mm tubes. Approximately 5 mg of chromium acetylacetonate was added to samples to decrease spin relaxation times. The spectra were measured at 100 °C using pulse repetition intervals of 5 s and gated proton decoupling. The glass transition, melting points and heats of fusion were determined by differential scanning calorimetry using a Perkin-Elmer DSC-7. The DSC scans were obtained by first heating copolymer samples to 200 °C for 10 min, cooling them to 20 °C at 20 °C per minute, aging them at room temperature for 24 h and then reheating from 0 °C to 200 °C at 20 °C/min. All DSC values in the tables are reheat values. Scans to determine the glass transition temperature were obtained by cooling the sample to -150 °C and then heating to 0 °C at 40 °C/min.

Mechanical tests were performed at 23 °C with ASTM D-1708 dumbbell specimens (2.2 cm gauge length) which were die cut from compression molded sheets of about 0.05 cm thickness. Crosshead separation rate was 25.4 cm/min for the three cycle 100% elongation test and 51 cm/min for the tensile and stress relaxation tests.

Tensile tests were run according to ASTM D638-96. Tensile modulus of elasticity was determined as the tangent slope at lowest strain. Elongation after break (percent elongation following break) was measured from benchmarks as immediate set of the center 10mm section of the specimen. The three cycle recovery test was performed by extension of the specimen three times to 100% elongation with a 30 second hold at each extension



and a 60 second hold at each recovery. Cumulative set after the first two cycles was measured from the strain at which stress exceeds the baseline on the third cycle. A stress relaxation test was also conducted by extension to 50% elongation and measuring the decay of the stress.

### Examples 12-17. Propylene Homopolymerization with Metallocenes 2, 4, 6-9.

The homopolymerization of propylene was carried out by Method A; results are reported in Table 1.

**Table 1. Propylene Polymerization with  
(2-Arylindenyl) Zirconocenes (2, 4, 6-9 / MAO).<sup>a</sup>**

Ex.	Catalyst <sup>b</sup>	Productivity <sup>c</sup>	%m <sup>4d</sup>	M <sub>w</sub> x10 <sup>-3 e</sup>	MWD <sup>e</sup>	ΔH <sub>m</sub> <sup>f</sup>
12	2/MAO	2 530	32	542	3.48	28
13	4/MAO	1 180	72	580	4.66	81
14	6/MAO	2 800	14	293	3.77	---
15	7/MAO	1 350	31	217	4.44	35
16	8/MAO	1 810	24	262	3.74	26
17	9/MAO	1 030	47	270	6.50	57

a) Reaction conditions: bulk propylene, 20 °C, [Zr] = 50 mM,  
[Zr] : [Al] = 1 : 1000, trxn = 30 min.;

b) 2 = (PhInd)<sub>2</sub>ZrCl<sub>2</sub>,  
4 = (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub>,  
6 = (PhInd)(1MePhInd)ZrCl<sub>2</sub>,  
7 = (PhInd)(1MebfmPhIn)ZrCl<sub>2</sub>,  
8 = (bfmPhIn)(1MePhInd)ZrCl<sub>2</sub>,  
9 = (bfmPhIn)(1MebfmPhIn)ZrCl<sub>2</sub>;

c) (kg·PP)/(mol·Zr·h);

d) determined by <sup>13</sup>C NMR;

e) determined by GPC;

f) determined by DSC

### Examples 18-26. Ethylene/Propylene Copolymerization with Metallocenes 1 and 4.

The copolymerization of ethylene and propylene was carried out according to Method B to give copolymers with ethylene contents of 60-75%; the results are reported in Table 2. Examples 18-20 are comparative examples prepared with a stereorigid metallocene 1; Examples 21-26 are carried out with catalysts of the present invention. Note the melting range for polymers prepared by catalysts of the present invention are

broader and the heats of fusion higher than polymers produced by comparative bridged catalyst 1.

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**Table 2. Ethylene/Propylene Copolymerization with Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> 1/MAO and (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub> 4/MAO.<sup>a</sup>**

Ex.	Catalyst <sup>b</sup>	T <sub>pol</sub> , °C	%E <sup>c</sup>	Melting range, °C <sup>d</sup>	T <sub>m</sub> , °C <sup>d</sup>	ΔH <sub>m</sub> , J/g <sup>d</sup>
18	1/MAO	0	66	110-132	124	0.55
19	1/MAO	0	68	110-134	127	1.9
20	1/MAO	0	75	110-134	125	0.17 <sup>e</sup>
21	4/MAO <sup>f</sup>	2	61	31-130 75-136	45, 118 123	14.5 <sup>f</sup> 7.1 <sup>g</sup>
22	4/MAO <sup>f</sup>	1	64	31-129 40-130	45, 119 123	16.8 <sup>g</sup> 13.5 <sup>e</sup>
23	4/MAO <sup>f</sup>	0	67	60-136	122	3.4
24	4/MAO <sup>f</sup>	0	69	28-133 40-132	45, 119 122	17.6 <sup>g</sup> 15.4 <sup>e</sup>
25	4/MAO <sup>f</sup>	0	69	30-131	42, 120	4.8
26	4/MAO <sup>f</sup>	23	60	27-126 30-127	44, 115 44, 115	5.4 14.1 <sup>e</sup>

a) Conditions: [Zr]=1-2 mM, [MAO]:[Zr]=10 000, t<sub>rxn</sub>=25 min, 60 mL liq. P. DSC sample preparation: annealed at 160-180 °C for 20 min, cooled to 25 °C over 2 h, aged for 24 - 36 h if not otherwise specified.

10

b) 1 = Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,  
4 = (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub>.

c) Mole % ethylene determined by <sup>13</sup>C NMR spectroscopy.

d) Determined by DSC.

e) Baseline curved, error may be present in peak area determination.

15

f) Two shown values correspond to two runs on different DSC samples prepared from the same polymer sample.

g) Samples aged for 1 mo.

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**Examples 27-79. Copolymerization of Ethylene and Propylene with Metallocenes 1, 2, 4, 6-9.**

Ethylene/Propylene Copolymerizations were carried out according to Method A; results are reported in Tables 3 and 4.

Table 3. First Order Markov Copolymerization Parameters for 1, 2, 4, 6-9 /MAO.

Ex.	Cat. <sup>a</sup>	T °C	N <sub>exp</sub> <sup>b</sup>	X <sub>e</sub> /X <sub>p</sub> in feed <sup>c</sup>	%E in polymer <sup>d</sup>	r <sub>e</sub> r <sub>p</sub> <sup>e</sup>	r <sub>e</sub> <sup>e</sup>	r <sub>p</sub> <sup>e</sup>
27	1/MAO	1±1	5	0.04 - 0.18	23 - 54	0.49±0.03	5.4±0.6	0.09±0.01
28	1/MAO	20±1	1	0.07	42	0.50	7.1	0.07
29	2/MAO	1±1	5	0.06-0.22	21 - 44	0.92±0.08	3.8±0.3	0.25±0.01
30	2/MAO	20±1	5	0.06-0.16	23 - 45	1.3±0.2	5.4±0.9	0.24±0.04
31	4/MAO	1±1	5	0.07-0.25	18 - 43	1.3±0.1	4.2±0.7	0.31±0.03
32	4/MAO	20±1	5	0.05-0.08	14 - 22	1.9±0.1	6.0±0.2	0.33±0.03
33	6/MAO	1±1	1	0.09	30	1.32	6.3	0.21
34	6/MAO	19±1	2	0.08-0.13	34 - 41	1.14±0.01	6.4±0.6	0.18±0.02
35	7/MAO	0±1	4	0.04-0.27	15 - 62	1.49±0.30	7.0±0.39	0.21±0.03
36	7/MAO	19±1	3	0.04-0.13	20 - 45	1.34±0.22	8.6±1.3	0.15±0.01
37	8/MAO	0±1	1	0.26	34	1.77	2.9	0.62
38	8/MAO	18±1	3	0.08-0.11	33 - 42	1.66±0.04	9.0±0.2	0.19±0.01
39	9/MAO	0±1	2	0.03 - 0.08	28 - 64	1.80±0.26	7.3±0.5	0.25±0.03
40	9/MAO	20±1	5	0.05-0.13	31-48	1.72±0.35	10.8±2.7	0.16±0.02

5

- a) 1 = Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,  
 2 = (PhInd)<sub>2</sub>ZrCl<sub>2</sub>,  
 4 = (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub>,  
 6 = (PhInd)(1MePhInd)ZrCl<sub>2</sub>,  
 7 = (PhInd)(1MebfmPhIn)ZrCl<sub>2</sub>,  
 8 = (bfmPhIn)(1MePhInd)ZrCl<sub>2</sub>,  
 9 = (bfmPhIn)(1MebfmPhIn)ZrCl<sub>2</sub>;

10

- b) number of experiments used for determination of the average reactivity ratios;  
 c) the range of the ratios of the mole fractions of ethylene (X<sub>e</sub>) and propylene (X<sub>p</sub>);  
 d) the range of mole % E in copolymers determined using <sup>13</sup>C NMR;  
 e) determined using <sup>13</sup>C NMR

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Note that the product of the reactivity ratios (r<sub>e</sub>•r<sub>p</sub>) for metallocenes of the present invention are in the range 1.1 < r<sub>e</sub>•r<sub>p</sub> < 1.8 whereas those for comparative metallocene 1 are less than 1 (r<sub>e</sub>•r<sub>p</sub> = 0.5).

**Table 4. Ethylene-Propylene Copolymers Generated with Catalysts 1,2,4 and 6-9/MAO.<sup>a</sup>**

Ex.	Catalyst <sup>b</sup>	T <sub>pol</sub> , °C	%E <sup>c</sup>	T <sub>g</sub> , °C <sup>d</sup>	Melt range, °C	T <sub>m</sub> , °C	ΔH <sub>m</sub> , J/g	M <sub>w</sub> •10 <sup>-3e</sup>	MWD <sup>e</sup>
41	1/MAO	0	0	—	20-160	143	125	70.6	2.0
42	1/MAO	2	11	-28	26-122	89	63	89.4	2.3
43	1/MAO	2	23	-39	25-90	58	9.3	78.1	2.1
44	1/MAO	2	42	-52	none	none	none	75.2	2.0
45	2/MAO	20	0	-8	30-160	140	31	542	3.5
46	2/MAO	20	9	-26	30-110	65	8	1 547	5.5
47	2/MAO	20	24	-26	none	none	none	1 312	3.6
48	4/MAO	0	0	—	20-160	147	100	756	5.7
49	4/MAO	2	9	-21	31-122	100	23	2 397	5.4
50	4/MAO	1	21	-31	31-142	45	2.2	2 292	4.2
51	4/MAO	1	33	-40	none	none	none	2 235	2.6
52	4/MAO	0	67	—	60-136	122	3.4		
53	6/MAO	20	0	—	none	none	none	293	3.8
54	6/MAO	18	34	-34	none	none	none	596	5.3
55	6/MAO	19	41	—	none	none	none	633	5.2
56	6/MAO	1	30	-33	none	none	none	1 225	3.1
57	7MAO	20	0	-3	30-157	140	35	217	4.4
58	7MAO	18	20	-22	28-80	50	3.6	334	6.0
59	7MAO	18	23	-25	26-84	46	5.6		
60	7MAO	19	29	-31	29-120	48	3.4	488	5.6
61	7MAO	19	45	—	none	none	none	342	3.7
62	7MAO	1	0	-4	30-159	140	32.2	367	3.3
63	7MAO	0	15	-16	55-109	66	2.6	655	3.4
64	7MAO	1	36	-36	none	none	none	845	3.1
65	7MAO	1	62	—	27-130	118	8.3	869	3.4
66	8/MAO	20	0	-3	30-158	145	26	262	3.7
67	8/MAO	17	33	—	none	none	none		
68	8/MAO	19	42	—	none	none	none	515	4.3
69	8/MAO	0	34	—	none	none	none	907	3.2
70	9MAO	20	0	-2.6	20-163	148	57	270	6.5
71	9MAO	20	31	—	61-125	73, 115	2.4	500	10.2
72	9MAO	20	33	-33	44-128	117	4.2	450	6.2
73	9MAO	20	38	—	52-124	62, 115	2.0	558	6.8
74	9MAO	20	43	—	39-126	116	1.75	495	8.8
75	9MAO	19	48	-43	21-123	47, 115	7.5	385	5.9
76	9MAO	20	70	-52	64-126	117	2.9	611	5.0
77	9MAO	0	28	-27	30-81	51	4.7	781	4.2
78	9MAO	0	64	-48	35-125	115	3.5	673	3.7

a) DSC sample preparation: annealed at 160-180 °C for 20 min, cooled to 25 °C over 2 h, aged for 36 h;

- 5 b) 1 = Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,  
2 = (PhInd)<sub>2</sub>ZrCl<sub>2</sub>,  
4 = (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub>,

6 = (PhInd)(1MePhInd)ZrCl<sub>2</sub>,

7 = (PhInd)(1MebfmPhIn)ZrCl<sub>2</sub>,

8 = (bfmPhIn)(1MePhInd) ZrCl<sub>2</sub>,

9 = (bfmPhIn)(1MebfmPhIn)ZrCl<sub>2</sub>;

5 c) Mole % E determined by <sup>13</sup>C NMR spectroscopy;

d) Half Cp extrapolated;

e) Determined by high temperature GPC.

10 Note that polymers prepared with metallocene 1 containing 42% ethylene (Example 44) are amorphous, whereas polymers of similar composition (48%E) derived from metallocene 9 (Example 75) are crystalline and exhibit a melting range of 21-123 °C with a heat of fusion of 7.5 J/g. Also note that propylene polymers obtained from metallocene 1 containing 23% ethylene exhibit a melting range of 25-90°C and ΔH<sub>m</sub> = 9.5 J/g (Example 43) whereas propylene polymers containing as much as 33% E derived from metallocene 9  
15 show higher melting range of 44-128°C with ΔH<sub>m</sub> = 4.2 J/g (Example 72).

The compositional heterogeneity of the copolymer sample of Example 78 was investigated by extraction in boiling heptane. The microstructures of the heptane soluble (50 wt%) and insoluble (50 wt%) fractions of Example 78 were analyzed by Solution <sup>13</sup>C NMR spectroscopy (Table 5). The ethylene contents (%E) of the fractions differ by 3% or  
20 less and the reactivity ratios calculated from the dyad distribution differ by less than 0.16 from the average of the whole polymer sample, clearly indicating the compositional homogeneity of these copolymers.

**Table 5. Fractionation of Ethylene Propylene Copolymer from Metallocene 9**

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Example	Sample	%Wt	%E <sup>a</sup>	r <sub>erp</sub>
78	Whole	100	64	1.54
	HS	50	61	1.46
	HI	50	64	1.70

a) determined by solution <sup>13</sup>C NMR

b) HS = heptanes soluble

c) HI = heptanes insoluble

### 30 Examples 79-104.

The copolymerization of ethylene and 1-hexene was carried out with metallocenes 1, 2, 4, 5 and 9-10 by Method C. The data and characteristics of the polymers are reported in Table 6.

35



**Table 6. Summary of the DSC and Molecular Weight Data for Ethylene-1-Hexene Copolymers Generated with Catalysts 1, 2, 3, 4, 9 and 10/MAO.<sup>a</sup>**

Ex.	Cat. <sup>b</sup>	T <sub>pol</sub> , °C	%E <sup>c</sup>	T <sub>g</sub> , °C <sup>d</sup>	melt range, °C <sup>a</sup>	T <sub>m</sub> , °C <sup>a</sup>	ΔH <sub>m</sub> , J/g <sup>a</sup>	M <sub>w</sub> •10 <sup>-3e</sup>	MWD <sup>e</sup>
79	1/MAO	19	54	-72	none	none	0	53	2.2
80	1/MAO	18	65	-76	none	none	0	52	2.1
81	1/MAO	19	69	—	none	none	0	61	2.2
82	1/MAO	18	77	-77	37-45	43	0.3	75	2.4
83	1/MAO	18	81	-74	33-43	40	4.7	71	2.2
84	2/MAO	18	54	-68	none	none	0	1176	3.2
85	2/MAO	18	59	—	none	none	0	1353	5.5
86	2/MAO	18	64	-72	none	none	0	1474	7.4
87	4/MAO	18	44	—	none	none	0	554	7.4
88	4/MAO	18	55	—	26-126	116	2.7	691	6.3
89	4/MAO	18	62	—	28-130	40, 120	8.0	994	7.6
90	4/MAO	18	66	—	61-81 82-124	63, 114	3.5	783	6.7
91	4/MAO	18	70	—	29-75 76-126	38, 121	4.2	1076	9
92	4/MAO	18	73	—	23-130	37, 119	16	826	6.3
93	4/MAO		80	-70	16-116	25, 86	15.7	1164	6.1
94	4/MAO		89	-59	11-117	20, 105	31	1318	4.6
95	4/MAO	18	100	—	100-145	133	136	1534	4.7
96	3/MAO	18	49	—	none	none	0	1793	2.8
97	3/MAO	18	62	—	30-50	40	1.0	1287	4.8
98	9/MAO	18	68	—	14-63 79-114	23, 96	2.7	646	5.1
99	9/MAO	18	70	—	40-68 92-120	22, 108	5.4	700	4.8
100	9/MAO	18	76	—	20-67 78-114	23, 107	4.0	901	5.8
101	9/MAO	18	79	—	15-43 79-114	20, 106	8.4	825	4.7
102	10/MAO	18	48	—	none	none	0	1193	4.1
103	10/MAO	18	55	-74	34-127	117	4.0	1335	7.8
104	10/MAO	17	64	-74	29-135	117	5.2	1758	7.9

a) DSC sample preparation: annealed at 200 °C for 10 min, cooled to 25 °C at 20 °C/min, aged 24 h.

b) 1 = Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,  
 2 = (PhInd)<sub>2</sub>ZrCl<sub>2</sub>,  
 4 = (bfmPhIn)<sub>2</sub>ZrCl<sub>2</sub>,  
 3 = (PhInd)<sub>2</sub>HfCl<sub>2</sub>,  
 9 = (bfmPhIn)(1MebfmPhIn)ZrCl<sub>2</sub>,  
 10 = (DTBM)<sub>2</sub>ZrCl<sub>2</sub>.

c) Mole % E determined by <sup>13</sup>C NMR spectroscopy.

d) Half Cp extrapolated (DSC).

e) Determined by high temperature GPC.

As indicated in Table 6, Comparative Examples 79-83, carried out with bridged metallocene 1 yields random ethylene/hexene copolymers. Polymers made with this metallocene containing 54 - 69 mol% ethylene are amorphous, exhibiting no melting point by DSC analysis as indicated by "none" under the melt range and  $T_m$  columns. In contrast, metallocene 4 of the present invention yields polymers containing 55 - 70% ethylene with melting points ranging from 26 - 130°C.

The properties of the ethylene/hexene copolymers of Example 92 and 93 are compared to representative other comparable polyolefin elastomers and reported in Table 7, Parts I and II. Comparative Example 105 is a commercial Ethylene/Octene Elastomer obtained from Dow (Engage 8200<sub>sm</sub>), Comparative Example 106 is an Ethylene/Butene Elastomer obtained from Exxon (Exact 4033<sub>sm</sub>), and comparative Example 107 is a polypropylene elastomer as described in Waymouth et al. US 5,594,080.

**Table 7, Part I Mechanical Properties of Polyolefin Elastomers.**

Polymer	Ex. 92	Ex. 93	Ex. 94	Comp. Ex 105	Comp. Ex 106	Comp. Ex 107
				Engage 8200	Exact 4033	polypropylene 37% mmmm
Comonomer	Hexene	Hexene	Hexene	Octene	Butene	None
Mole % Ethylene	73	80	89	87	89	0
PE Melt Index	nd	nd	nd	5.0	0.8	
Mw ( $\times 10^3$ )	826	1164	1318	77.4	nd	386
$T_m$ range (°C)	23-130	16-116	11-117	20 - 70	20 - 70	40-160
$T_m$ peak (°C)	119	25, 86	20-105	66	64	148
$\Delta H_m$ (J/g)	16.2	15.6	31	10.5	13.7	
$T_g$ (°C) <sup>a</sup>	—	-66	-60	-54	—	
Density (g/cc)	0.8682	0.8694	0.8819	0.87	0.88	0.8663
Tensile Strength (MPa)	3.6	4.2	8.8	9.6	16.9	12.3
Tensile Modulus (MPa)	2.9	4.0	10.3	6.9	12.3	8.9
Elongation at Break (%)	565 $\pm$ 62	428	360	1130	750	830
Elongation after Break (%)	90 $\pm$ 17	26	57	300	210	34

a) Determined by Dynamic Mechanical Analysis.

Table 7, Part II Mechanical Properties (cont'd.)

<b>100% Elongation 3 Cycle Test:</b>	<b>Ex. 92</b>	<b>Ex. 93</b>	<b>Ex. 94</b>	<b>Comp. Ex 105</b>	<b>Comp. Ex 106</b>	<b>Comp. Ex 107</b>
% stress relaxation, 30 s, 1st cycle	33	17	17	23	23	39
% retained force, 2nd cycle	24	41	29	28	20	29
% set, cumulative	19	13	13	13	11	7
<b>Stress Relaxation Test</b>						
50% elongation, 5 min	51	33	25	28	28	48

As evident from Table 7, all polyolefin elastomers have a similar density and comparable elastomeric properties. However, the copolymer elastomers of Example 92 and 93 have a particularly useful combination of properties that includes a low glass transition temperature ( $T_g = -70^\circ\text{C}$ ) and melting ranges that extend to  $130^\circ\text{C}$ . Note in particular that while the copolymers of Example 92, and comparative Examples 105 and 106 have similar degrees of crystallinity as manifested by their heats of fusion ( $\Delta H_f$  (J/g) from 10.5 - 16.2), the melting point of the copolymer of Example 92 is  $119^\circ\text{C}$ . It is unexpected that this high melting point is achieved at a much lower mol % ethylene (73 mol % versus 87 or 89 mol %).

The compositional heterogeneity of these copolymers was investigated by extracting the copolymers in boiling ether and hexanes. The results of these fractionation experiments on the copolymer samples of Example 90 and 91 are reported in Table 8.

**Table 8. Fractionation of Ethylene/Hexene Copolymers from Metallocene 4**

Example	Sample	%Wt	%E <sup>a</sup>	T <sub>m</sub> , °C	Melt Range, °C
90	Whole	100	66	63, 114	61 - 81, 82 - 124
	ES <sup>b</sup>	16	59	42	35 - 50
	EI	84	72	41, 118	29 - 126
	EI/HxS <sup>c</sup>	80	69	45	25 - 85
91	Whole	100	70	39, 119	29 - 75, 76 - 126
	ES <sup>b</sup>	23	63	35	30 - 43
	EI <sup>c</sup>	77	73	35, 119	24 - 129
	EI/HxS <sup>c</sup>	64	67	34, 119	27 - 126
	HxI <sup>e</sup>	13	75	35, 59, 117	24 - 128

5 a) determined by solution <sup>13</sup>C NMR. b) ES = diethylether soluble. c) EI/HxS = diethylether insoluble/hexane soluble. d) HxI = hexane insoluble.

Note that the mole fraction of ethylene in the various fractions of the copolymer are all within 10% of the mean mole percent ethylene of the copolymer sample, indicating that these materials have a narrow composition distribution.

10

#### **INDUSTRIAL APPLICABILITY:**

It is evident that the polymers of the present invention, and the polymerization catalysts and processes by which the polymers are produced will have wide applicability in industry, *inter alia*, as elastomers having higher melting points than currently available elastomers, as thermoplastic materials, and as components for blending with other polyolefins for predetermined selected properties, such as raising the melting point of the blend. As noted in Table 7 and the accompanying discussion, typical polymers of this invention, while they have degrees of crystallinity similar to that of Dow's Engage 8200<sub>tm</sub> and EXXON's 4033<sub>tm</sub>, they have a broader melting point range that extends to higher temperatures, e.g., to 130°C, and above.

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It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. We therefore wish this invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

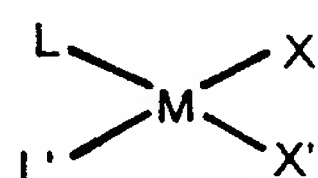


**We Claim:**

1. A method of producing an olefin copolymer from a feedstock including ethylene and at least one alpha olefin monomer comprising in any suitable sequence the steps of:

5 a) contacting said feedstock with an unbridged, rotating, non-rigid fluxional metallocene catalyst component in the presence of a co-catalyst for a time sufficient to produce an elastomeric thermoplastic copolymer;

b) said unbridged fluxional metallocene catalyst component is selected from at least one compound of the formula:



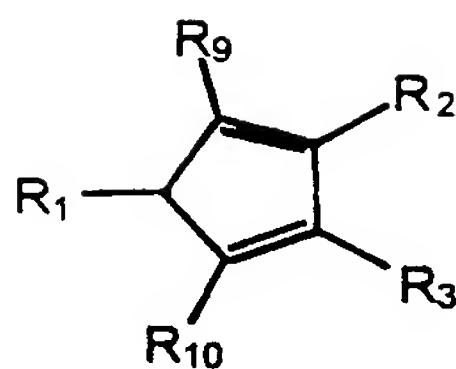
10 in which M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide; X and X' are the same or different uninegative ligands; and L and L' are ligands selected from the same or different substituted, polynuclear, hydrocarbyl, and hetero-hydrocarbyl rings;

15 c) said L and L' ligands are selected so that the fluxional metallocene component isomerizes between at least two coordinate geometry states that have different reactivities toward at least one of ethylene and said alpha olefin while in the respective coordinate geometry states; and

d) recovering an elastomeric copolymer product.

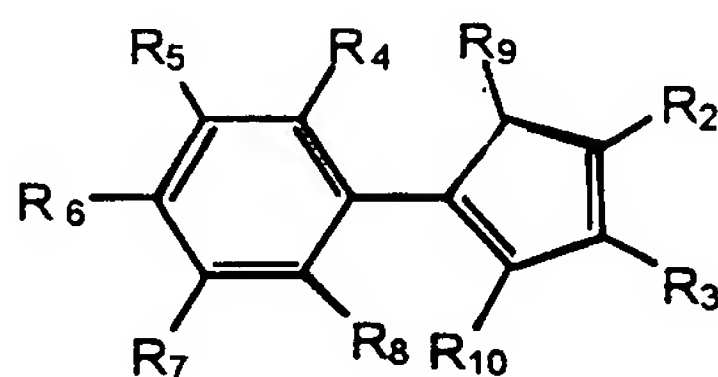
2) A polymerization process as in claim 1 wherein: said substituted rings are selected from cyclopentadienyl, heterocyclopentadienyl and indenyl rings; said uninegative ligands are selected from hydride, halogen, hydrocarbyl, halohydrocarbyl, amine, amide, or borohydride ions; said Transition Metal is selected from Titanium, Hafnium, Vanadium, 5 and Zirconium; said Group 3 metal is Yttrium; said Lanthanide is Samarium; and said Actinide is Thorium.

3) A polymerization process as in claim 2 wherein said cyclopentadienyl and heterocyclopentadienyl rings have the formula:



where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>9</sub>, and R<sub>10</sub> are selected from the same or different hydrogen, alkyl, alkylsilyl, aryl, alkoxyalkyl, alkoxyaryl, alkoxysilyl, aminoalkyl, aminoaryl or substituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms and where said ring is heterocyclopentadienyl, the hetero atom of said ring is selected from N, P, As and B.

4) A polymerization process as in claim 3 wherein said ligands L and L' are selected cyclo-pentadienes of the general formula:



where R<sub>2</sub> through R<sub>10</sub> are the same or different hydrogen, alkyl, alkylsilyl, aryl, alkoxyalkyl, alkoxyaryl, alkoxysilyl, aminoalkyl, aminoaryl or substituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms.

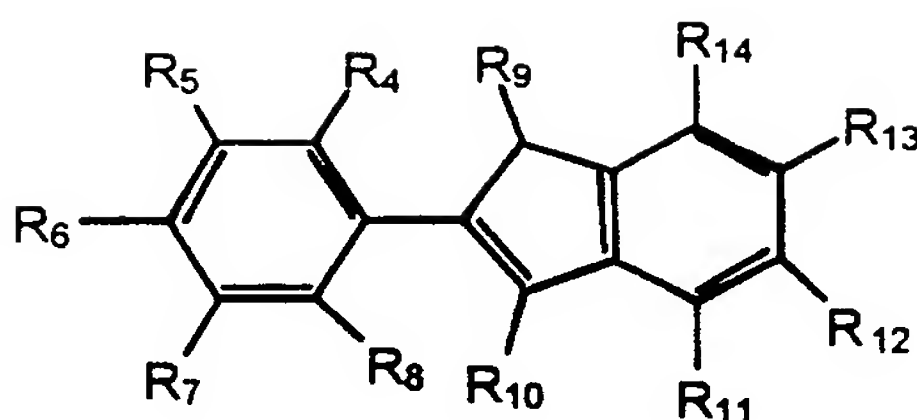
5) A polymerization process as in claim 4 wherein said cyclopentadiene is selected from 3,4-dimethyl-1-phenyl-1,3-cyclopentadiene (R<sub>2</sub>=R<sub>3</sub>=CH<sub>3</sub>, and R<sub>6</sub>=H), 3,4-dimethyl-1-p-tolyl-1,3-cyclopentadiene (R<sub>2</sub>=R<sub>3</sub>=CH<sub>3</sub>, and R<sub>6</sub>=CH<sub>3</sub>), 3,4,-dimethyl-1-(3,5-bis(trifluoromethyl)phenyl)-1,3-cyclopentadiene (R<sub>2</sub>= R<sub>3</sub>=CH<sub>3</sub>, and R<sub>6</sub>=CF<sub>3</sub>), and 3,4-dimethyl-1-(4-*tert*-butylphenyl)-1,3-cyclopentadiene (R<sub>2</sub>= R<sub>3</sub>=CH<sub>3</sub>, and R<sub>6</sub>=tBu).

6) A polymerization process as in claim 3 wherein R<sub>1</sub> is an aryl group and R<sub>2</sub> and R<sub>3</sub> are connected as part of a ring of 3 or more carbon atoms.

7) A polymerization process as in claim 6 wherein said aryl group is selected from phenyl, biphenyl and naphthyl groups.

8) A polymerization process as in claim 6 wherein said aryl group is a 2-aryl indene of

the formula:



where  $R_4$  through  $R_{14}$  are selected from the same or different hydrogen, halogen, aryl, hydrocarbyl, silahydrocarbyl and halo-hydrocarbyl substituents.

9) A polymerization process as in claim 8 wherein said 2-aryl indene is selected from 2-phenylindene; 1-methyl-2-phenyl indene; 2-(3,5-dimethylphenyl) indene; 2-(3,5-bis-trifluoromethylphenyl) indene; 1-methyl-2-(3,5-bis-trifluoromethylphenyl) indene; 2-(3,5-bis-tertbutylphenyl) indene; 1-methyl-2-(3,5-bis-tertbutylphenyl) indene; 2-(3,5-bis-trimethylsilylphenyl)indene; 1-methyl-2-(3,5-bis-trimethylsilylphenyl)indene; 2-(4-fluorophenyl) indene; 2-(2, 3, 4, 5-tetrafluorophenyl) indene; 2-(2, 3, 4, 5, 6-pentafluorophenyl) indene; 2-(1-naphthyl) indene; 2-(2-naphthyl) indene; 2-[(4-phenyl)phenyl] indene; and 2-[(3-phenyl) phenyl] indene.

10) A polymerization process as in claim 1 wherein at least some of the resulting copolymer product is fractionated into at least one fraction selected from an ether soluble, a hexanes soluble, and a hexanes insoluble fraction, and the mole fraction of ethylene in the various fractions of the copolymer are substantially within 15% of the mean mole percent ethylene of the initial resultant copolymer product.

11) A polymerization process as in claim 1 wherein the copolymer produced is selected from thermoplastic polymers having a molecular weight distribution,  $M_w/M_n$ ,  $\leq 10$ ; a composition distribution  $\leq 15\%$ ; a melting point of  $\geq$  about  $90^\circ\text{C}$ ; a melting point index of  $\geq$  about  $80^\circ\text{C}$ ; a glass transition temperature of  $\leq$  about  $-20^\circ\text{C}$ ; a mole fraction of crystallizable component,  $X_c$ , of from about 30% to about 99%; and elastomeric properties.

12) A polymerization process as in claim 10 wherein said copolymer fractions are in the range of about 0% to about 70% by weight of said ether soluble fraction, from about 0% to about 95% of said hexanes soluble fraction and from about 0% to about 95% of said hexanes insoluble fraction.

13) A polymerization process as in claim 12 wherein said hexanes soluble fraction has a melting range of up to about 125°C, and said hexanes insoluble fraction has a melting range up to about 142°C.

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14) A polymerization process as in claim 11 wherein said copolymer has a weight average molecular weight,  $M_W$ , in excess of about 1 million.

15) A polymerization process as in claim 11 wherein said copolymer has a molecular weight distribution,  $M_W/M_n$ ,  $\leq 8$ .

16) A thermoplastic olefin copolymer having a molecular weight distribution,  $M_W/M_n$ ,  $\leq 10$ ; a composition distribution  $\leq 15\%$ ; a melting point of  $\geq$  about 90°C; a melting point index of  $\geq$  about 80 °C; a glass transition temperature of  $\leq$  about -20 °C; a mole fraction of crystallizable component,  $X_c$ , of from about 30% to about 99%;  
5 and elastomeric properties.

17) A thermoplastic olefin copolymer as in claim 16 which comprises from about 0% to about 70% by weight of an ether soluble fraction, from about 0% to about 95% of a hexane soluble fraction, and from about 0% to about 95% of a hexane insoluble fraction.

18) A thermoplastic ethylene/alpha olefin copolymer as in claim 17 wherein said hexanes soluble fraction has a melting range of up to about 125°C, and said hexanes insoluble fraction has a melting range up to about 142°C.

19) A thermoplastic olefin copolymer as in claim 16 which has a weight average molecular weight,  $M_W$ , in excess of about 1 million.

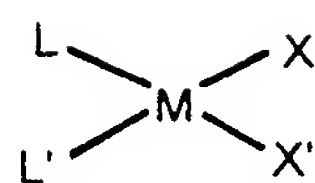
20) A thermoplastic olefin copolymer as in claim 16 which has a molecular weight distribution,  $M_W/M_n$ ,  $\leq 8$ .

21) A thermoplastic olefin copolymer as in claim 20 which has a molecular weight distribution,  $M_W/M_n$ ,  $\leq 6$ .

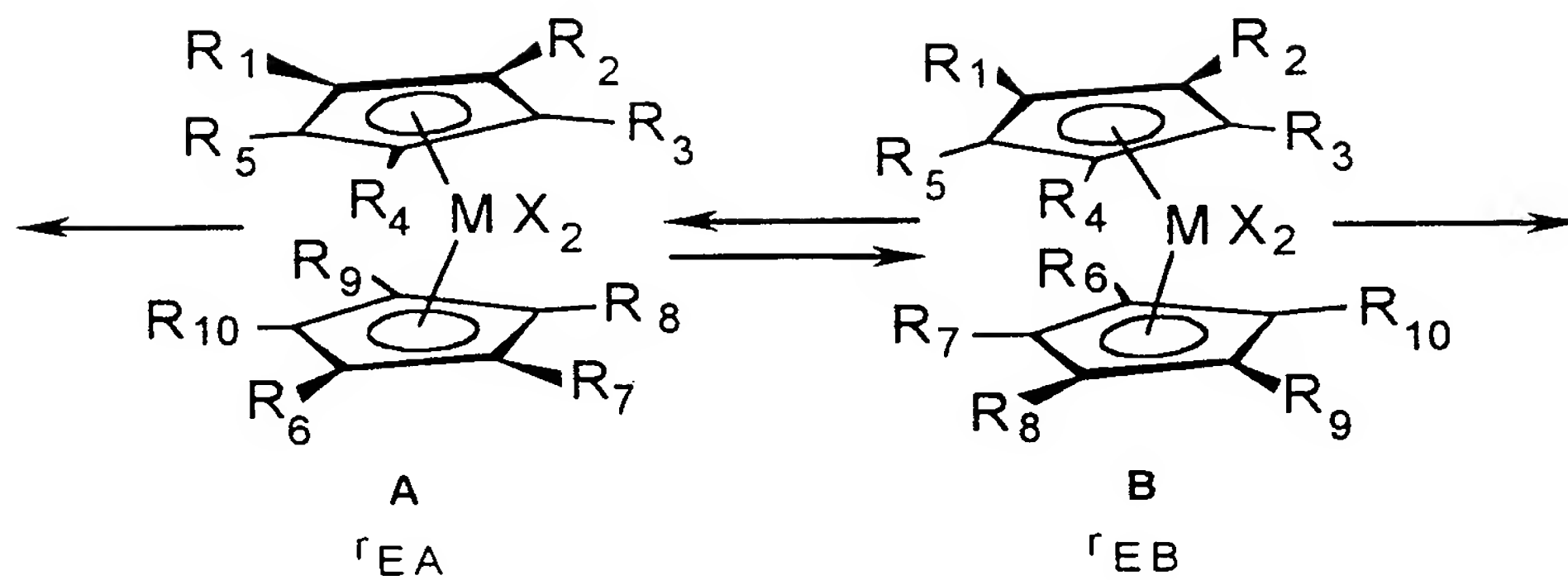
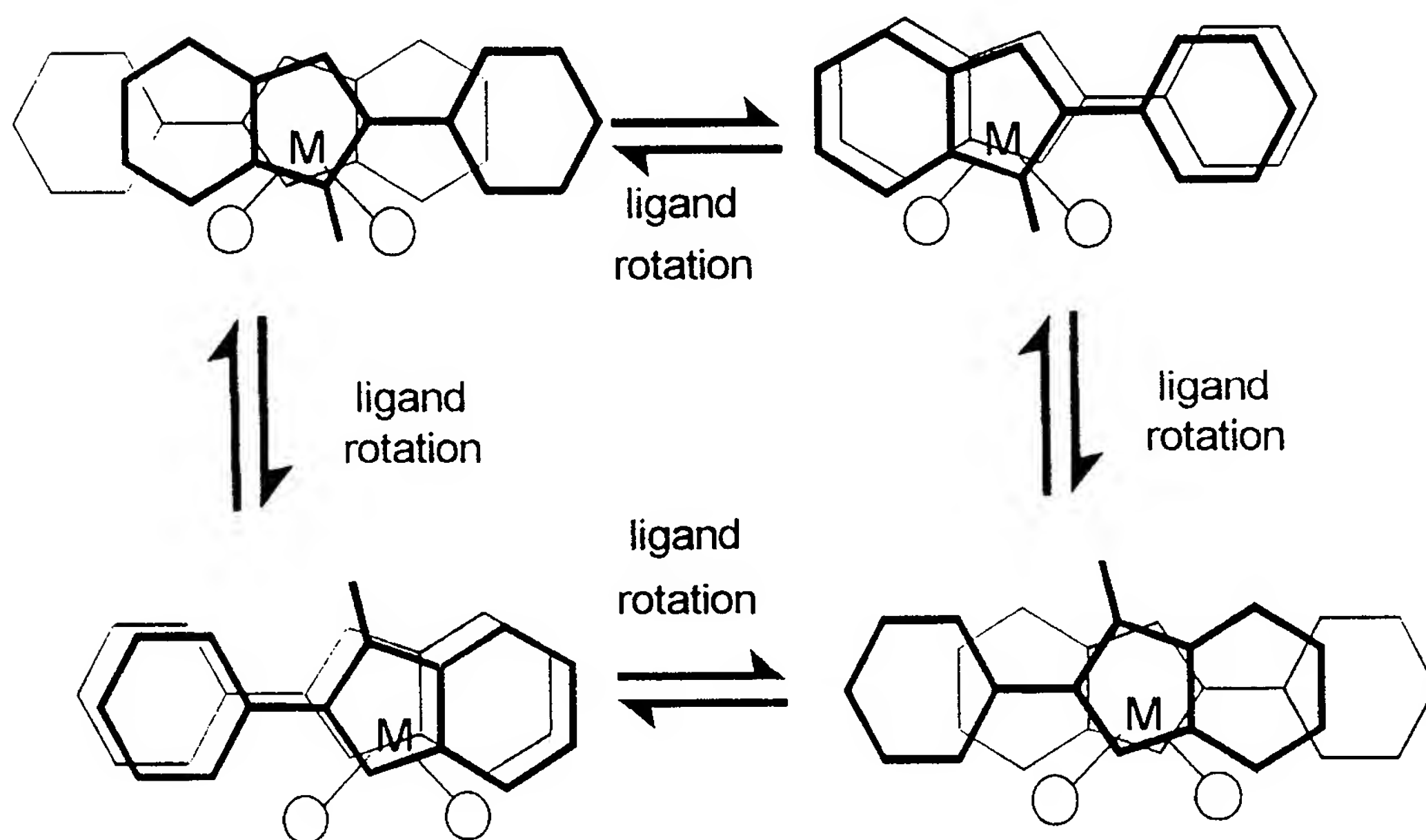
22) A thermoplastic olefin copolymer as in claim 16 wherein the comonomers are selected from ethylene and alpha olefins.

23) An unbridged fluxional metallocene catalyst component which exhibits plural coordination geometries for olefin polymerization, having the formula:





wherein M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide; X and X' are the same or different uninegative ligands, and said ligands L and L' are selected from at least one of : (1-methyl-2-phenylindenyl)-(2-phenylindenyl); (1-methyl-2-phenylindenyl)[2-(3,5-bis-trifluoromethyl-phenyl)indenyl]; 1-methyl-2-(3,5-bis-trifluoromethylphenyl)-indenyl-(2-phenylindenyl); [1-methyl-2-(3, 5-bis-trifluoromethylphenyl)indenyl][2-(3, 5-bis-trifluoromethylphenyl)-indenyl]; and (1-methyl-2-phenylindenyl)[2-(3,5-bis-tertbutylphenyl)indenyl] groups.

**FIG. 1****FIG. 2**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/00540

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 4/64, 8/00, 10/06

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/322; 526/79, 87, 126, 127, 134, 160, 170, 348.5, 348.6, 348.11, 352; 556/11, 53

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,594,080 A (WAYMOUTH et al) 14 January 1997.	1-23
A	US 5,192,732 A (DURANEL et al) 09 March 1993.	1-23
A	US 5,055,535 A (SPITZ et al) 08 October 1991.	1-23

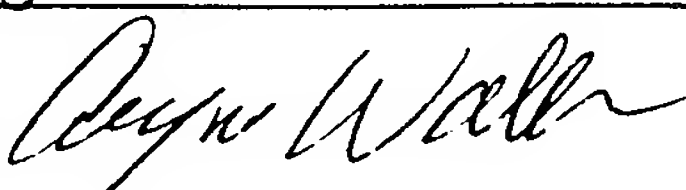


Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 14 MARCH 1999	Date of mailing of the international search report 23 MAR 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BERNARD LIPMAN  Telephone No. (703) 308-0661

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/00540

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

525/322; 526/79, 87, 126, 127, 134, 160, 170, 348.5, 348.6, 348.11, 352; 556/11, 53